

I.

Osmotic Pressure of Solutions
of Cane-Sugar.

II.

A Study of Zinc Ferrocyanide as a
Semi-Permeable Membrane
for the Measurement of
Osmotic Pressure.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

WILLIAM LEE KENNON.

BALTIMORE, MD.

1906.

THE ESCHENBACH PRINTING CO.
EASTON, PA.

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CONTENTS.

Acknowledgment	4
Historical Introduction.....	5
I. The Osmotic Pressure of Solutions of Cane-Sugar.....	8
The Cell.....	8
The Manometer.....	11
(a) Calibration.....	14
(b) Capillary Depression.....	18
(c) Filling the Manometer.....	18
(d) Closing the Manometer.....	19
(e) Determination of the Total Air Volume.....	22
The Control of Temperature Conditions....	23
Correction for Inversion.....	26
Correction for Dilution of Cell Contents.....	31
Other Corrections.....	32
General and Theoretical Considerations.....	34
Experimental Part.....	36
Summary of Results.....	60
Conclusions.....	64
II. A Study of Zinc Ferrocyanide as a Semi-Permeable Membrane for the Measurement of Osmotic Pressure.....	65
Introductory Remarks.....	65
Experimental Part.....	67
Summary of Results.....	77
Conclusions.....	77
Biography.....	79

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HISTORICAL INTRODUCTION.

The discovery by M. Traube¹ in 1867 of the artificial preparation of semi-permeable membranes led, ten years later, to the classic quantitative measurements carried out by W. Pfeffer², upon which van't Hoff³ based the brilliant generalizations presented in his epoch-making paper, "Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen." The conclusions of van't Hoff immediately gave the subject profound importance. Notwithstanding this, however, and the recognition of the meagre character of Pfeffer's measurements, which only extended over a small range of concentrations, the highest of which was less than one-fifth normal, very little has been done since in the direct measurement of osmotic pressure. The cause of this is to be found in the enormous difficulties which must be overcome.

The problem was later attacked by indirect means, which led to the valuable results obtained by De Vries,⁴ Tammann,⁵ Hamburger⁶ and many others, to which reference can hardly be made here.

Methods of direct measurement have, however, been under investigation in a systematic manner in this laboratory for the last five years. Notwithstanding the brilliant character of the initial work, space can only be given here to a brief account of the development of the work carried out in this laboratory, though a discussion of the earlier views will be taken up in their proper place in the light of the results of the present investigation.

Pfeffer's method of preparation of semi-permeable membranes was beset, as is well known, with most serious difficulties; so much so, that almost all efforts on the part of others even to repeat his work have resulted in failure. Evidently, then,

¹ Archiv. f. Anal. und Physiol., p. 87 (1867).

² Osmotische Untersuchungen, Leipsic (1877).

³ Z. physik. Chem. 1, 481 (1887).

⁴ *Ibid.*, 2, 415 (1888).

⁵ Wied. Ann., 34, 299 (1888).

⁶ Z. physik. Chem., 6, 319 (1890).

a new method had to be devised far more reliable than Pfeffer's, if any marked advance was to be made in the direct measurement of osmotic pressure. It was just this discovery in 1901, by Morse and Horn,¹ that gave an impetus to the work in this laboratory. They found that if a solution of a copper salt and one of potassium ferrocyanide are separated by a porous wall which is filled with water, and a current passed from an electrode in the former to another electrode in the latter solution, the copper and ferrocyanogen ions meet on or within the porous wall and form a semi-permeable membrane of very great strength. Moreover, the method furnished a rapid and most reliable means of preparing such membranes.

In subsequent work by Morse with Frazer, Carver,² Coony,³ and Hall,⁴ the method has been extended to the preparation of many other precipitates. About twenty-five have been studied, which show decided osmotic activity.

The next problem presenting itself was in securing the manometer in the cell. This, however, was not of a serious character and was satisfactorily solved by Morse and Frazer⁵ in essentially the manner now in use, which will be discussed when the construction of the cells used in this work is described.

After means of firmly securing the manometer had been found, the further testing of the electrically deposited membranes developed another source of weakness, namely, the porous clay wall of the cell. This proved to be the most formidable difficulty encountered up to the present. It was evident that no quantitative measurements of pressure, or even the further study of the strength and efficiency of the membranes, were possible until suitable walls for the support of the membrane could be obtained. This problem was at once taken up by Morse and Frazer⁶ and by Morse and Hall,⁷ and since continued by Morse and Frazer. Although a number of cells of almost

¹ Am. Chem. J., 26, 80.

² B. F. Carver, Dissertation, Johns Hopkins Univ. (1903).

³ J. P. Coony, Dissertation, Johns Hopkins Univ. (1903).

⁴ E. S. Hall, Dissertation, Johns Hopkins Univ. (1904).

⁵ Am. Chem. J., 28, 1.

⁶ Am. Chem. J., 28, 1.

⁷ E. S. Hall, Dissertation, Johns Hopkins Univ. (1904).

ideal texture and strength have been prepared and used in this laboratory the problem may still be said to be under investigation, and the recent work of Morse and Frazer,¹ as well as the present investigation may be regarded in a sense, as bearing thereon.

The obvious source of weakness in the first cells experimented with was their coarse texture and softness. Cells made of finer materials, hard-burned, were then prepared. These gave better but far from satisfactory results.

The problem was then taken up on a broader basis. Cells of various kinds and mixtures of clays, fashioned into shape in different ways, and burned to different degrees of hardness were prepared and experimented with. Thin sections of those yielding the best results were studied under the microscope to determine the quality of texture, and attempts to reproduce those qualities that seemed essential by changes and modifications in the methods previously used, led, after four years of persistent effort, to the preparation of the porous cups now in use.

With the manufacture of suitable porous walls, walls that must withstand pressures upwards of 200 kilograms per square inch, the last obstruction to the direct measurement of osmotic pressure was removed, and this problem was immediately undertaken by Morse and Frazer,² with the results recently published.

Even at this stage of the investigation it was expected that further problems would present themselves before the measurements could be pushed to the greatest refinement; and also that minor improvements in the construction of the various parts of the apparatus, as well as the introduction of certain factors of correction, would be suggested by experience. Such proved to be the case. Possibly the most serious of these difficulties was the so-called "Thermometer effects," which resulted from the inability to avoid sudden changes in temperature. The effect of this difficulty in maintaining uniform temperatures will be considered when the manner in which it has been overcome is taken up.

¹ Am. Chem. J., 34, 1.

² *Ibid.*

Other difficulties which proved very troublesome, resulted from several defects in the construction of the manometer. These have now been obviated in a perfectly satisfactory manner. Means have also been devised for the more careful study of any changes that might take place in the solution within the cell during the course of the experiment. These, together with many other improvements and modification, suggested by experience, have rendered the repetitions of the previous experiments desirable, because the aim, which has been steadily kept in mind since the study of osmotic pressure was first begun in this laboratory, has been to place the measurements on as accurate and firm a basis as possible, in order to throw the greatest possible light on the nature of these phenomena and to fix the laws which describe their course.

I

THE OSMOTIC PRESSURE OF SOLUTION OF CANE-SUGAR.

*The Cell.*¹

The construction of the several parts of the cells used in this investigation, as well as the manner in which these parts are assembled, have only been altered in very slight detail from that already fully described:² It will only be necessary therefore, to give a brief resumé here.

The cell indicated by A in Fig. I. is of cup-shaped form, about 9 cm. in length, having a rim at the open end with a thickness equal to that of the cell wall. The exterior diameter of the cell, just below the rim, is about 3.55 cm.; diameter of opening, 2.5 cm. The interior and exterior diameters of the cell are a little less at the closed end, the cell possessing a slight taper of 0.044 centimeter per centimeter of length. On burning, these dimensions shrink about 10 per cent.

The cell, after burning, is mounted in a specially constructed

¹ It has been considered advisable to go somewhat into details regarding the construction, form and calibration of the apparatus and of the procedure in carrying out the experimental work, since in measurements of the character recorded in this work, it is these features which determine to a large extent the trustworthiness of the results.

² Am. Chem. J., 34, 1.

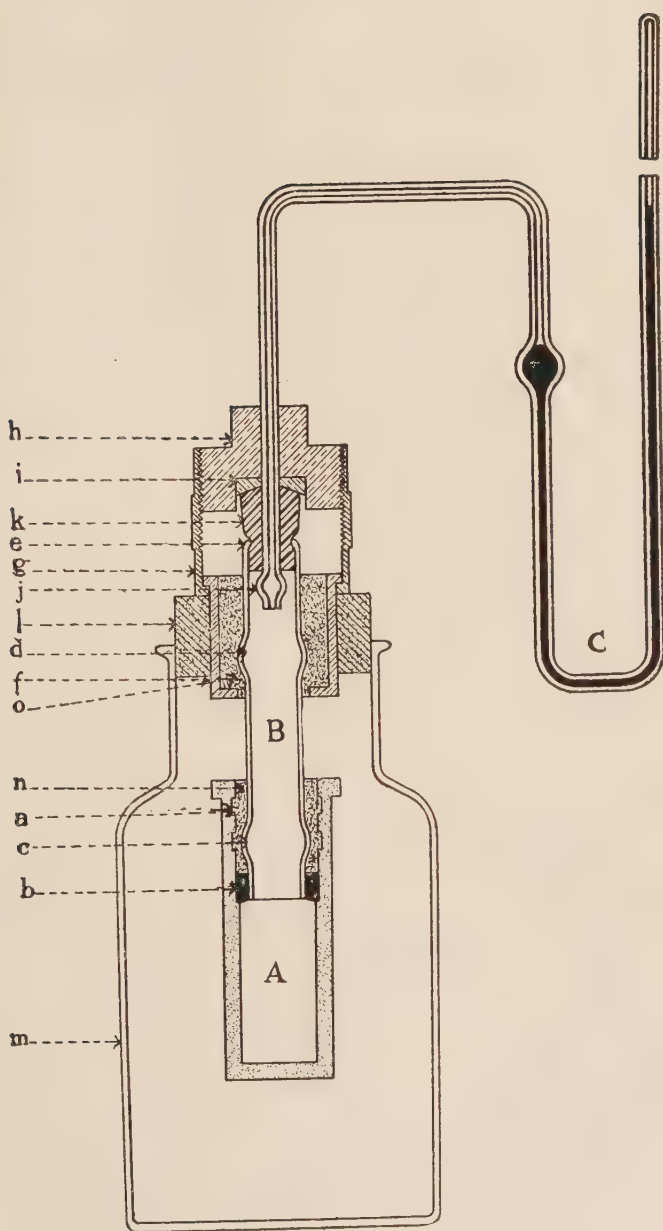


Fig. I.

chuck.¹ While slowly turning, the interior is ground for about one-third the length of the cell by a rapidly rotating carborundum wheel attached to the tool carriage of the lathe, until a slight shoulder is formed around its entire interior. Two grooves are then cut, one of which is designated by *a* in the figure. In case the diameter of the rim is too great to admit of free passage through the brass shoulder, *g*, it is ground to the proper diameter before the cell is removed from the chuck.

The glass tube, B, Fig. I., which serves for the attachment of the manometer to the cell, was made of thick hard glass tubing about 1.42 centimeters in diameter, which was tested thoroughly as to toughness and other necessary qualities. However, at best, this is by far the weakest and most unsatisfactory part of the entire apparatus, and the greatest care should be taken in selecting the tubing of which it is made. Nearly every accident encountered in the prosecution of this work was due to the breaking of the glass tube, either while under pressure or during manipulation. All efforts in the past to substitute a tube of porcelain or other material for the glass tube proved unsuccessful.

The tube should be as near cylindrical as possible. Two bulbs, *d* and *c*, should be blown at the positions shown and the neck constricted somewhat. The tube should be of such length as not to have the top of the cell and the bottom of the brass shoulder, *o*, over 1.5 centimeters apart.

This having been accomplished, the soapstone washer, *b*, is constructed in the following manner: A piece of soapstone about three inches in length, with a cross section greater than that of the cell, is placed in a chuck on the lathe and turned until it has a diameter slightly greater than that of the opening of the cell. A hole is then bored in the centre somewhat smaller than the glass tube, and afterwards carefully turned until it perfectly fits the end of the glass tube, upon which it is to be placed. The outside of the soapstone cylinder is then carefully turned until it fits in the cell and rests firmly on the shoulder within. The end of the hollow soapstone cylinder is then beveled inward to an angle of about 30°, so as to prevent the

¹ Am. Chem. J., 28, 16.

lodgment of air when the cell is filled. The end of the soapstone cylinder is then cut off to the proper length so as to fit that portion of the glass tube below the bulb. The reason for selecting soapstone for the manufacture of this washer was because its coefficient of expansion was about the same as that of the material of the cell, and, also, because it can be easily worked on the lathe. Hard rubber and other substances have proved unsatisfactory.

The three essential parts of the cell having been constructed, the next step is to secure them together. The soapstone ring or washer is fitted over the end of the glass tube with the beveled end outward. While the tube is in an inverted position, molten shellac is placed around the joint between the glass and the soapstone, and over the end of the washer. The tube, still in the inverted position, is placed in an air bath and heated at 110° for five hours, and at 115° for one hour. This is done to cement the washer to the glass tube and to raise the melting point of the shellac.

The glass tube carrying the washer is then fixed in the cell in the following manner:

The interior of the cell down as far as the shoulder and the entire exterior of the soapstone disk, are carefully painted several times with rubber solution, which is prepared by fusing black rubber tubing and dissolving it in carbon bisulphide to a consistency which will not spread too rapidly. While the rubber is still soft, the glass tube with washer attached is firmly set in place. It is well in this operation to hold the cell in an inverted position, so as to prevent any rubber, which is likely to be scraped off the cell wall, from running down the interior of the cell and thus injuring the porous wall on which the membrane is afterwards to be deposited. After the tube and washer are in place, the interior wall of the upper part of the cell is again painted with rubber solution, for fear that some of the rubber may have been rubbed off while inserting the tube and washer. It is very necessary to have the portion of the cell wall above the washer completely covered with rubber,

because, if any sugar solution or water were to diffuse through the porous clay wall into the cement which is placed in the space between the glass tube and the cell wall, the cement would be rapidly disintegrated and the cell ruined.

The cell, after these operations, is again placed in the air-bath and heated at about 110° until the rubber is hard, but not brittle. This usually requires about ten hours. At this point it has been found advisable though it was not previously done in the construction of the cells, to place a little solid shellac on top of the washer between the glass tube and the cell wall, and again heat at 110° for several hours. When the cell is cool the space between the glass tube and the cell wall, represented by *n* in Fig. I., is filled with litharge cement. This cement, made to a consistency which will pour slowly, is prepared from litharge, made by heating lead carbonate, and glycerine, containing 10 per cent water. The handling of the cement must be done rapidly, as it hardens quickly. After the cement has set, it is painted with the rubber solution on the upper exposed surface. The cement should have eight or ten days to set hard before the cell is subjected to pressure. However, it will harden sufficiently in ten or twelve hours to admit of careful handling of the cell. It is then well to cement the brass piece *o*, having an exterior flange at the top, in place. This should be done so that the glass tube will be in its center. It is also important to have the upper bulb of the glass tube embedded in the cement, and to leave the neck of the tube extending about 6 mm. above the cement. The exposed surfaces of the cement are also painted with rubber solution.

As soon as the cement has had sufficient time to harden, the cell is in condition to have the air driven from the cell wall, and the membrane deposited, which processes will be described later.

The Manometer.

The form of manometer is in general that used by Morse and Frazer, and designated by C in Fig. I., though several important improvements have been made in its construction. These will be considered somewhat in detail.

The manometer as represented in the diagram possesses several objectionable features, which became evident when it was put in use in pressure measurements.

In what has been described as the "strenuous manipulation" of inserting the stopper carrying the manometer, a portion of the enclosed air will pass around the arm and render the re-filling of the manometer necessary (an operation which delays work very much), unless the pressure exerted on the stopper, which must be considerable, is uniform and maintained throughout the entire operation. To avoid this, another bulb was blown in the ascending limb of the manometer, as shown in Fig. IV.

Again, most serious difficulties were encountered in making readings of the pressures indicated in the manometer, owing to the uncertainty in reading the top of the air column. The cause of this was found in the irregular conical form of the top of the air space formed when the end of the manometer was sealed. Also, the necessary softening of the glass in fusing the end of the manometer gave rise to an uncertainty as to the bore of the upper end of the manometer. As the entire length of the air column is only 15 or 20 mm. under pressures of solutions near the normal, it is evident that these difficulties become serious, where high pressures are to be measured.

The ideal arrangement would be to fill the upper end of the manometer with a short mercury column, but this was not easy of accomplishment. As mentioned by Morse in this regard, "In the few cases where we have tried it, we found that the separation of the necessary mercury thread involved a roughness of manipulation which appeared to endanger the instrument. Moreover, we were unable to effect a sufficiently complete dislodgment of the air from the space which the mercury should fill." The problem was not given up, however, and after many plans were proposed and abandoned, the very result hoped for was achieved, and in a perfectly satisfactory and expeditious manner.

The manner in which this was accomplished will be considered in detail under the head of closing the manometer.

One other alteration in the construction of the manometer must be mentioned here. The open end of the manometer

should be enlarged as shown at *j*, Fig. I. This is necessary to prevent the end of the manometer when under pressure from being pushed through the stopper. It also serves to spread the stopper, in case of any upward movement of the manometer, and thus the stopper is pressed more firmly against the constricted neck of the tube. This forms a perfectly tight and, when the stopper is properly supported, a very firm joint. It is advisable, however, that this enlargement be made without the bulb shown in the figure. The reason for this is that air bubbles frequently get into the capillary bore between the bulb and the bend in the arm, or even around into the bulb on the descending arm. When there is no bulb at *j*, such air bubbles can be easily removed by immersing the end of the manometer in a vessel of water, tilting the manometer slightly, and then by diminishing the pressure on the water, the air is drawn out of the end of the manometer, when, on restoring the diminished pressure, the arm is completely filled with liquid. A simple form of apparatus had been devised for accomplishing this.

This apparatus also facilitates the replacing of a solution of one concentration by that of another. It further renders possible the replacement of mercury, which is often lost from the bulb in manipulation.

It is evident that this increased facility in the manipulation of the manometer is rendered possible by the presence of the bulb in the ascending arm. The manometer carries a nut, *h*, in which the limb of the manometer should have slight play. This nut is threaded externally to fit the interior threads of the brass collar, *g*, which slips over and catches the flange of the shoulder, *o*. The nut does not slip over the enlargement on the end of the manometer, and, of course, should be placed on the tube before the enlargement is made.

The horizontal arm of the manometer should be of sufficient length to give room for the hand while inserting the manometer in the cell.

The manometers used in this investigation had two lines of reference etched on them and designated below as scratches No. 1 and No. 2, or upper and lower scratch, respectively, with

reference to the top of the manometer. Finally, the internal bore of the tubing used in the construction of the manometers was about 0.5 mm. The total length of each manometer was about 60 cm. The reasons for selecting these dimensions have been fully set forth¹.

(a) *Calibration.*

When the construction of the manometer is completed, the next step is its calibration.

The method employed for this purpose was to measure the length of a short mercury thread placed end to end at successive intervals throughout the length of the manometer tube. The apparatus by means of which this was accomplished is shown in Fig. II. In brief, it consists of a hard rubber cylinder, *b*, in which the glass tube, *i*, is set with litharge cement. An iron rod is threaded into the cylinder as shown.

To carry out the calibration, the glass tube, *i*, as well as the entire manometer, is filled with pure mercury. The mercury is then drawn down the bore of the manometer a short distance, and the short thread, *h*, is introduced. The thread should be between 12 and 15 mm. in length. The air space between the thread and the main column of mercury should not exceed 2 mm. The entire apparatus is then firmly fixed in a vertical position, a short distance in front of a cathetometer carrying a telescope provided with micrometer eye-piece, and near a vertical standard meter. The calibrating apparatus, cathetometer and meter scale are all mounted on the same foundation, which does not come in contact with the floors or woodwork of the laboratory.

The mercury column in the manometer is then drawn down till the lower end of the thread, *h*, is exactly opposite the line of reference near the bottom of the free arm of the manometer, and indicated by *g*. The line of reference and the upper end of the thread are then read by means of the telescope and meter bar, thus ascertaining the length of the thread in that part of the tube just above the lower line of reference. The thread is then moved by turning the threaded bar until the lower end of the thread rests in exactly the same position as was previously occupied by

¹ Am. Chem. J., 34, p. 3.

its upper end. The hair of the telescope is then placed on the new position, and the reading taken. Thus, the length of the thread in the new position is determined; also, the length of the thread in successive portions of the tube is measured throughout the entire length of the manometer. When the top of the manometer is reached, the thread is again drawn down to the lower reference line and all the readings repeated. If consistent values for the length of the thread in the same portion of the tube are obtained in the second set of readings, the average of the two sets of values will be quite accurate enough. If the second values do not check with the first, the readings should be repeated until the experimenter is satisfied that he has correct values for the length of the thread.

The thread is now run out of the manometer tube, is caught in a weighing tube, and its weight is accurately found. Also, the weight of the column of mercury filling the entire calibrated portion of the manometer is found.

In the calibration of the manometers used in this work the average of two series of values was taken in each case. The calibration data of one of these manometers is given below. This data is made convenient for use by reduction to a calibration unit and by being plotted in the form of a curve.

Table A.

Calibration Data of Manometer, No. 6.

No. of reading.	Readings upward on scale.		Readings upward on scale.	
	First series.	Differences.	Second series.	Differences.
I.	II.	III.	IV.	V.
1	867.54	13.61	867.54	13.61
2	853.93	13.58	853.93	13.58
3	840.35	13.65	840.35	13.67
4	826.70	13.69	826.68	13.68
5	813.01	13.62	813.00	13.63
6	799.39	13.64	799.37	13.61
7	785.75	13.60	785.76	13.58
8	772.15	13.56	772.18	13.56
9	758.59	13.61	758.62	13.66
10	744.98	13.75	744.96	13.68
11	731.23	13.75	731.28	13.73
12	717.48	13.63	717.55	13.75
13	703.85	13.74	703.80	13.72

Table A—(Continued).

Calibration Data of Manometer, No. 6.

No. of reading. I.	Readings upward on scale.		Readings upward on scale.	
	First series. II.	Differences. III.	Second series. IV.	Differences. V.
14	690.11	13.65	690.08	13.65
15	676.46	13.72	676.43	13.72
16	662.74	13.74	662.71	13.71
17	649.00	13.71	649.00	13.75
18	635.29	13.72	635.25	13.70
19	621.57	13.75	621.55	13.76
20	607.82	13.81	607.79	13.78
21	594.01	13.86	594.01	13.85
22	580.15	13.86	580.16	13.81
23	566.29	13.92	566.35	14.05
24	552.37	13.87	552.30	13.88
25	538.50	13.90	538.42	13.85
26	524.60	13.88	524.57	14.01
27	510.72	13.89	510.56	14.06
28	496.83	14.06	496.50	14.10
29	482.77	14.10	482.40	14.02
30	468.67	14.06	468.38	14.03
31	454.61	14.11	454.35	13.98
32	440.50	14.16	440.37	14.07
33	426.34	14.21	426.30	14.18
34	412.13	14.21	412.12	14.12
35	397.92	14.13	398.00	14.19
36	383.79	14.16	383.81	14.21
37	369.63	14.17	369.60	14.20
38	355.46	...	355.40	...

Calibration Data of Manometer, No. 6.

No. of readings.	Average of differences of first and second series.		Product of num- ber of settings by mean length of thread.	
	VI.	VII.	VIII.	Correction values. IX.
1	13.610	13.61	13.841	0.23
2	13.580	27.19	27.682	0.49
3	13.660	40.85	41.523	0.67
4	13.685	54.53	55.364	0.83
5	13.625	68.16	69.205	1.05
6	13.625	81.78	83.046	1.27
7	13.590	95.37	96.887	1.52
8	13.560	108.93	110.728	1.80
9	13.635	122.57	124.569	2.00

Table A—(Continued).

Calibration Data of Manometer, No. 6.				
No. of readings.	Average of differences of first and second series.	Readings on scale calculated from zero-point.	Product of number of settings by mean length of thread.	Correction values.
	VI.	VII.	VIII.	IX.
10	13.715	136.28	138.410	+2.13
11	13.740	150.02	152.251	+2.23
12	13.690	163.71	166.092	+2.38
13	13.730	177.44	179.933	+2.49
14	13.650	191.09	193.774	+2.68
15	13.720	204.81	207.615	+2.81
16	13.725	218.54	221.456	+2.92
17	13.730	232.26	235.297	+3.04
18	13.710	245.98	249.138	+3.16
19	13.755	259.73	262.979	+3.25
20	13.795	273.53	276.820	+3.29
21	13.855	287.38	290.661	+3.28
22	13.835	301.22	304.502	+3.28
23	13.985	315.20	318.343	+3.14
24	13.875	329.08	332.184	+3.10
25	13.875	342.95	346.025	+3.08
26	13.945	356.90	359.866	+2.97
27	13.975	370.87	373.707	+2.84
28	14.080	384.95	387.548	+2.60
29	14.060	399.01	401.389	+2.38
30	14.045	413.06	415.230	+2.17
31	14.045	427.10	429.071	+1.97
32	14.115	441.22	442.912	+1.69
33	14.195	455.41	456.753	+1.34
34	14.165	469.58	470.594	+1.01
35	14.160	483.74	484.435	+0.70
36	14.185	497.92	498.276	+0.36
37	14.185	512.11	512.117	+0.01

Other data regarding this manometer, which have been used in the computation of pressures, are as follows:

Distance between scratches equals 298.06 mm.

Height of top of manometer above bottom scratch equals 503.91 mm.

Weight of mercury thread used in this calibration equals 0.0620 gram.

Average radius of bore of manometer tube equals 0.32 mm.

Exterior diameter of manometer tube equals 5.1 mm,

Volume of the manometer above bottom scratch equals 0.16 cc.

Correction for meniscus equals 0.21 calibration unit.

It will be observed from Table A that the total space covered by the mercury thread while setting it end to end throughout the length of the tube was 512.11 mm., and that 37 settings were made. The mercury thread, therefore, filled an average length of space of 13.841 mm. The thread was then regarded as containing 13.841 calibration units. Referring to Table A, column VII., contains the readings on the meter scale, which would have been obtained if the zero of the scale had coincided with that of the manometer. Column VIII. gives multiples of the volume or of the calibration units contained in the mercury thread corresponding to the readings in column VII. The differences are given in column IX. and represent the corrections which must be applied at the 37 points in order to transfer actual readings into calibrated or volume readings.

These corrections were plotted on a curve, a line representing the manometer being used as the axis of abscissas.

The other manometers used in this work were calibrated in exactly the same manner. On account of the large amount of space required, the calibration data of these manometers will not be given.

In the calibration of manometer No. 4, the mercury thread contained 15.264 calibration units and weighed 0.0409 gram. The average radius of its bore was 0.25 mm. The correction equals for meniscus 0.17 calibration unit.

In the calibration of manometer No. 5, the average length of the mercury thread equals 15.685 calibration units. Weight of thread equals 0.0385 gram. Distance between scratches equals 293.94 mm. Height of top of manometer above bottom scratch equals 482.58 mm. Correction for meniscus equals 0.16 calibration unit.

(b) *Capillary Depression.*

Before the manometer is filled with dry air and sealed, the capillary depression of the mercury in its arm is determined.

(c) *Filling the Manometer.*

To fill the manometer it is connected at its lower end by

means of a long thick-walled rubber tube, with a reservoir of mercury. The upper end is attached to the air-drying apparatus. This latter consists of a succession of tubes through which the air is drawn before it enters the manometer. The first tube which the air enters is filled with calcium chloride. It next passes into a tube partially filled with glass beads moistened with sulphuric acid, then into a tube of potassium hydroxide, next over ordinary phosphorus pentoxide and finally into a tube filled with glass wool into which has been condensed re-sublimed phosphorus pentoxide. The glass tube attached to the end of this train of absorption tubes and which is connected by means of a short thick rubber tube to the upper end of the manometer, contains a two-way stop-cock, which serves to connect the interior of the manometer either with the air-drying apparatus or with the atmosphere.

By lowering the reservoir, supposing the manometer tube to be completely filled with mercury at the start, the bore may be drawn full of air from the drying apparatus. The two-way stop-cock is then turned so as to place the interior of the manometer in communication with the atmosphere, when, by raising the reservoir, the air just drawn into the bore is expelled. The manometer may again be placed in communication with the drying apparatus and filled with air drawn over the absorbents as before, etc. This operation, which should be performed slowly, is repeated from forty to fifty times to insure the complete removal of moisture, carbon dioxide and ammonia from the air finally enclosed in the manometer.

(d) *Closing the Manometer.*

The closing of the manometer in such a manner as to leave a short mercury thread in its upper end, to avoid softening any of the calibrated part, which is afterwards to contain the air, and to avoid vitiating the enclosed air to any extent, constitutes one of the most valuable improvements in the construction of the apparatus.

The manner in which this has been accomplished is as follows: As the reservoir of mercury is lowered for the last time in filling the manometer, before all the mercury is drawn past the rubber connection, joining the end of the manometer to

the drying apparatus, the rubber tube is pinched to one side out of line with the manometer. This serves to break a small globule of mercury apart from the main column. By thus holding the rubber connection while the reservoir is lowered, the manometer may be filled with pure air from the drying apparatus drawn past the globule of mercury. Now, when the proper volume of air is drawn into the manometer, the rubber connection is allowed to resume its natural position. This brings the globule over the opening of the manometer and by further lowering the reservoir it may be drawn into the bore. Owing to the capillary depression of mercury in the small bore of the manometer tube, some diminished pressure is necessary before the mercury will enter it. After the globule is drawn in, the diminished pressure must be quickly restored or else the thread of mercury may run entirely through the tube to the bulb. The thread of mercury being drawn in after the air column, it is in general not of the desired length. It is usually too long, though of course it may be too short, in which case the operation must be repeated and a larger globule pinched off. If it is too long it may be run back to the top and pinched off until it is of the proper length. This, however, is very troublesome, as it usually happens that when the end of the thread is forced out of the top of the manometer, due to difference in capillary depression, the whole of the thread is forced out in an instant. The writer has found from his experience that a far more satisfactory method of shortening the mercuric thread is to draw it slowly down the entire length of the manometer column until one end enters the bulb, and the portion above the bulb is of the desired length, when, by gently tapping the bulb, the portion entering the bulb is broken off and falls across to the main supply of mercury. Of course, the entire volume of air originally introduced is now enclosed in the bulb. In the manometer used, threads of about 20 mm. length were employed.

The thread having been adjusted to the proper length, it is now run up the manometer column. When it is within 50 or 60 mm. of the top, the reservoir is fastened in position. The end of the manometer is placed in connection with the

atmosphere through the stop-cock and the joint with the air-drying apparatus is loosened. A piece of tubing of the same character as that of which the manometer is constructed, is fused on the end, and the manometer tube is softened just below the joint and drawn out into a fine capillary. This capillary is then scratched with a file and broken off at a height of 12 or 15 cm. above the end of the manometer. After the end of the manometer and the capillary have cooled, and, it might be added, that after every heating, the part should be thoroughly annealed, the reservoir is raised and the mercury thread forced up into the capillary until it fills it almost completely. The end of the capillary is then sealed.

At this point the interior of the manometer is under slight pressure, which was necessary to force the mercury thread into the fine capillary. This must be relieved before the attempt is made to soften the glass at the end of the manometer. In fact, the reservoir should be lowered until there is some diminished pressure on the air column amounting to 10 or 15 cm., so that when the end of the manometer is softened for the purpose of sealing, there will be a slight tendency for the walls to collapse.

The sealing of the end is accomplished in the following manner: After warming the joint of the capillary tube and manometer, it is touched with the fine point of the blow-pipe flame. This breaks the mercury column and volatilizes some of the mercury, the thread being forced some distance down the tube by the pressure of the mercury vapor. The tube is now softened and the capillary fused off, the end of the manometer being sealed and rounded down. The heated portion is allowed to cool slowly and if, while it is still somewhat soft, a little pressure is placed on the contents of the manometer by raising the reservoir slightly, the fine point of the cone formed at the top may be rounded, and, on cooling, the mercury vapor will condense and the thread will rise and fill the end completely.

Some patience and skill is required in carrying out this operation, though after a few trials the experimenter is generally able to perform it in a perfectly satisfactory manner.

The mercury thread thus secured in the top of the manometer

is not easily dislodged. After its distance from one of the lines of reference is once accurately determined, it may be regarded as the reference point itself. This has been done in the present experiment, thus facilitating considerably the operation of measuring pressures.

(e) *Determination of the Total Air Volume.*

The volume of air enclosed in the manometer must be accurately measured under known conditions of temperature and pressure. For this purpose the mercury reservoir is replaced by a tube of the same internal diameter as the manometer tube. A piece of the same specimen of tubing from which the manometer was constructed will best answer this purpose.

The whole apparatus is now placed before the cathetometer. When a uniform temperature has been secured, readings are made of the level of the mercury in the manometer, in the side-tube, and also in the top of the manometer. The barometer is then read and the temperature of the room taken. These readings should be made both before and after the other readings. Several sets of such observations should be taken, and from them is determined the volume under standard conditions, 0° , 760 mm. pressure occupied by the air enclosed in the manometer.

At this point the distance between the lines of reference, and the difference between the top and one line of reference, should be accurately determined once for all, for convenience of computation in the future.

The rubber tube connected with the end of the manometer is now removed, the end painted with rubber solution and a rubber stopper of proper size, the wall of the perforation of which is also covered with rubber solution, slipped over the end and fixed in place just above the enlargement on the end of the manometer. A fresh stopper must be used every time the manometer is used, and should be fixed in place at least 24 hours before the experiment is begun. The greatest care should be exercised in selecting stoppers of sufficient firmness, and to see that they are perforated in the centre. The coating of soap-stone which they have should be removed before they are used.



Fig. III.

The Control of Temperature Conditions.

The "thermometer effects", produced by sudden changes in temperature, already referred to, were the most serious obstacles which had to be contended with in the measurements of pressure by Morse and Frazer. The explanation of fluctuations in the height of the mercury column in the manometer when the temperature is changing is given by Morse¹ as follows: "When the temperature is falling, the solution and the mercury enclosed in the cell contract faster than the water can get through the membrane for the purpose of maintaining the pressure which is normal to the solution; and the mercury column, therefore, descends to an abnormally low point in the manometer. On the other hand, when the temperature of the room rises, the enclosed solution and the mercury expand faster than the water is expelled from the cell and the consequence is, that the mercury column in the manometer rises to a point which is abnormally high for the concentration of the solution."

If, after a change, the temperature remains constant for some time, the normal pressure will be registered, but the adjustment takes place very slowly, so where temperature is fluctuating, even slowly, abnormal pressures are usually indicated by the manometer.

The means which have been used to overcome this difficulty are very elaborate and are considered in detail in a communication from Morse and Frazer in the *American Chemical Journal* (July, 1906).

In general, however, they consist of: (1) a large well-protected bath containing about 300 litres of water, which is kept in constant motion; (2) an air compartment above the bath and in free communication with it, the air in which is kept circulating through pipes lying beneath the water in the tank below; and (3) variously automatically regulated electric and gas stoves which serve to maintain uniform temperatures outside the bath.

The temperature bath together with many other pieces of apparatus employed in this work are shown in the photograph, Fig. III. It is a rectangular wooden box, in length 1.24 meters,

¹ Am. Chem. J., 34, 24.

width 45.7 cm., and depth 66 cm. The bath proper is lined with tinned copper and is surrounded on the exterior by a large wooden box of such dimensions that the distance between them is not less than 75 mm. at any point. The intervening space is tightly packed with hair.

The air compartment above the tank expands, as shown in Fig. III., over about three-fourths the bath, leaving room at the end for the machinery, used to keep the water and air in the tank in circulation. It is provided with a top, *d*, hinged at the back, and with a mirror plate-glass window, *e*, in front, also hinged to the tank. These serve for opening the bath for the introduction of the cell with manometer attached.

To arrange for a measurement, the cell with manometer attached, fixed in the bottle containing the solvent, with which the cell is surrounded, as shown at *c*, is placed in the can, *a*, which is supported by an iron plate resting on the edges of the tank. The can covered with a hair pad, through a slit in which the manometer passes, is weighed down by the iron cylinder, *b*, weighing about 8 kilograms, which also serves for the even distribution of the heat to the bottle and its contents. The iron cans, plates, cylinders, etc., are painted with aluminum paint to provide against corrosion. This arrangement can be seen by referring to Fig. IV.

Thus, the cell, when a measurement is in progress, rests some distance below the surface of the water while the manometer column extends into the air compartment above. Hence, the liquids in the cell tend to take on the temperature of the water while the air in the manometer assumes the temperature of the air.

The plates supporting the cans are perforated for the introduction of the thermometers, which indicate the temperature of the water in the bath. Thermometers are also introduced through the top for registering the temperature of the air. These thermometers are graduated to $0^{\circ}.2$ and have been carefully compared with a thermometer calibrated at the Reichsanstalt.

For the circulation of the water, the following arrangement is provided: A lead pipe of 30 mm., internal diameter, joined

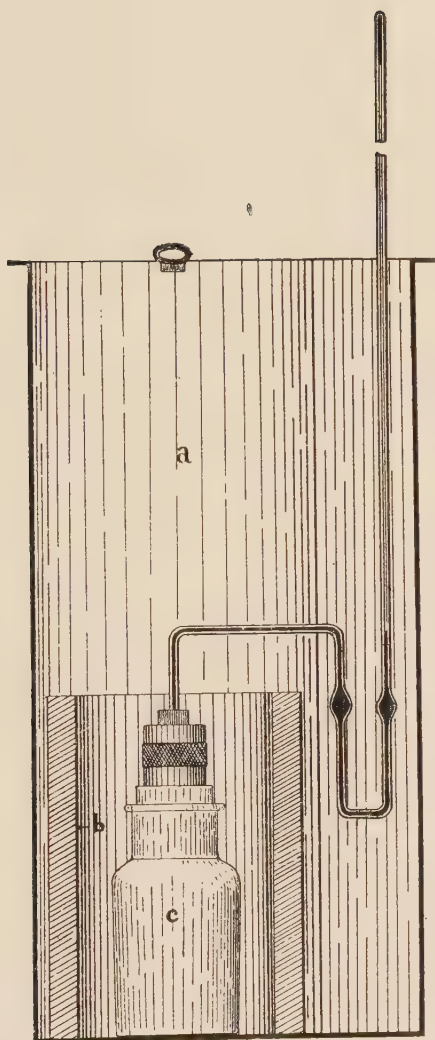


Fig. IV.

to a larger brass pipe at its upper end and terminating just below the surface of the water, runs down the side of the tank and along its bottom to the other end. Another pipe, arranged in much the same way, though terminating above the surface of the water, passes down the end of the tank to the bottom, where it divides and passes to either corner of the other end of the tank, where it rises and terminates near the top of the air compartment, as shown at *i* and *h*. Operating within the brass portion of the water pipe is a screw propeller drawing the water from the bottom of the far end of the tank and delivering it at the surface beneath the machinery, and in the air shaft a fan rotates and draws the warmer air from the upper part of the compartment and delivers it at the surface of the other end of the tank. This arrangement for circulating the air through pipes immersed below the water was designed with a view of maintaining both the air and water at as nearly the same temperature as possible.

The machinery by which the pump and fan are operated is situated above the tank, at the left in the photograph, and outside the air compartment. The propeller and fan are rotated by means of two flat discs faced with leather, mounted on a horizontal shaft connected by a belt with the motor below. The speed of the fan and propeller can be varied through wide ranges. The most satisfactory speeds have been found to be about 800 rotations per minute for the propeller and 2500 for the air fan. All this machinery is accurately constructed and runs smoothly and for long periods with little attention.

The air compartment is protected from communication with the atmosphere by a heavy enamel coating over the interior, and by providing all joints around the window and top with weather strips. The plate-glass window is further provided with a hair padded curtain, sections of which can be opened for the purpose of reading the manometers and thermometers. Illumination is secured by means of light from an incandescent lamp, thrown in from the exterior.

To provide against fluctuations in temperature without the the tank, the whole, *i.e.*, tank, cathetometer, etc., is surrounded by a canvas house 3.3 meters in length, 2 meters in width, and

2.6 meters in height, within which the observer stands while taking observations. The temperature of this small room is controlled quite accurately by automatic electric and gas stoves shown in Fig. III at *l* and *n*, respectively. These stoves are arranged so as to maintain a given temperature between small limits by means of regulators, as shown at *j* and *m*.

The distribution and support of the various parts of the measuring apparatus may be seen in Fig. III, where *f* is the cathetometer, *g* the standard meter scale, etc.

This equipment has solved, in quite a satisfactory manner, the control of temperature conditions. The data recorded in the experiments tabulated in the experimental part of this work show how closely this condition has been controlled. A few observations will be mentioned, however, for illustration. Thus, in Experiment 1, 0.1 weight-normal, Table I., there was a variation of only $0^{\circ}.1$ in the temperature of the water and of $0^{\circ}.5$ in the temperature of the air during a period of 18 hours. The temperatures of the air and water were the same at the beginning of the experiment, but were $0^{\circ}.6$ apart at its conclusion. This is a fair example of the records on temperatures.

Correction for Inversion.

Another difficulty which has to be contended with in the measurement of pressures of cane-sugar solutions is the small amount of inversion which takes place in the cell during the course of the experiment. Heretofore, the amount of this inversion has been determined by means of Fehling's solution. This proved very unsatisfactory on account of the very small quantity concentrations of invert-sugar that must be dealt with.

The adaptation of the saccharimeter to the determination of this inversion has proved a satisfactory means of dealing with the problem.

The instrument used in this work is the Schmidt and Haensch¹ half-shade saccharimeter with tripple field and double quartz-

¹ For detailed description, see Schmidt and Haensch: *Beschreibung und Gebrauchs-anweisung zu den Polarisations Apparaten* (1896), and their *Spezial-Preisliste* (1902).

wedge compensation. Illumination is produced by means of a small six-volt incandescent lamp of Haensch and Schmidt. Objectionable rays are cut off and a uniform field procured by placing between the source of light and the polarizer an absorption cell of potassium bichromate solution. The end point is determined by equality of shade.

The scale of the instrument is the Ventzke-Soleil. One hundred degrees on this scale corresponds to $34^{\circ}.55$ (D ray), and $39^{\circ}.10$ (j ray) on the circular scale.

The scale carries a vernier, and readings may be made to one-tenth of a degree. The "normal solution" for the instrument is one containing 26.048 grams of cane-sugar, weighed in air with brass weights, in 100 Mohr cubic centimeters at $17^{\circ}.5$. Such a solution produces a rotation of 100° when polarized in a two-decimeter tube.

For the details of the adaptation of this instrument to the determination of the inversion that takes place in a solution during a measurement of osmotic pressure, by simply determining the difference in rotation of a reserved portion of the original solution and of the solution taken from the cell after the pressure measurement, reference is made to the dissertation, Johns Hopkins University (1906), of Mr. E. J. Hoffman, in collaboration with whom the theoretical tables below were worked out and by whom they were verified experimentally.

The general plan of these calculations will be indicated briefly.

The solutions of which the osmotic pressures were measured, were made up on the weight-normal basis, *i. e.*, a gram-molecular weight, and sub-multiples on the hydrogen basis, of cane-sugar were dissolved each in 1000 grams of water, all weighings reduced to vacuum.

A solution containing 26.077 grams of sugar in 100 cc. of solution at 20° , made up in a flask calibrated for 20° , produces the same amount of rotation as the above "normal solution;" that is, when polarized in a two-decimeter tube it produces a rotation of 100° , or 1° rotation corresponds to 0.26077 gram of sugar in 100° cc. This solution contains 23.68 per cent of sugar. A 0.9 weight-normal solution contains 23.41 per cent of sugar. The *specific* rotatory power of cane-sugar solutions does not

change appreciably for even greater differences in concentration than this, so the same value 66.52 is taken for the "standard solution" and the 0.9 weight-normal solution. This value was calculated from Tollens'¹ formula.

$$[\alpha]_{\text{D}}^{20} = 66.386 + 0.015035 p + 0.0003986^2$$

Where p = percentage of sugar.

Therefore, in a 0.9 weight-normal solution of cane-sugar each degree of rotation corresponds to 0.26077 gram in 100 cc. rotated at 20° in a two-decimeter tube.

The specific rotatory power of invert-sugar was deduced from Gubbe's formula.

$[\alpha]_{\text{D}}^{20} = -19.657 - 0.0361 c$, where c = number of grams invert-sugar in 100 cc. The mean concentration, $c = -19.67$, of invert-sugar in our experiments was used.

The ratio of the specific rotatory power of invert-sugar to that of cane-sugar is found to be 0.2957, or 1 gram of invert-sugar produces the same rotation, in opposite direction, that 0.2957 gram of cane-sugar produces. This enables us to calculate that the invert-sugar resulting from the inversion of 0.26077 gram of cane-sugar will produce a laevo-rotation of 0°.311.

Consequently, if 0.26077 gram of cane-sugar is inverted in a 0.9 weight-normal-solution, there will be a loss of 1° in rotation, due to the loss of the cane-sugar, and a further loss of 0°.311, due to the laevo-rotation of the invert-sugar formed. Thus, a loss of 1°.311 in 100 cc. of a 0.9 weight-normal solution corresponds to the presence of 0.2745 gram, (the amount of invert-sugar formed by the inversion of 0.26077 gram of cane-sugar) of invert-sugar, or 1° loss equals 0.2093 gram invert-sugar in 100 cc.

In the same way, the amount of inversion corresponding to a loss of 1° in rotation in solutions of other concentrations may be ascertained. The result of such calculations are shown in Table B.

¹ Ber. d. chem. Ges., 10, 1403 (1877); Landolt: "Optische Drehungsvermögen."

² *Ibid.*, 18, 2207; Z. V. R bz-Ind., 1884; 1345, Landolt: "Optische Drehungsvermögen."

It will be seen that the change in this value for the range of concentrations with which we have had to deal is too small to be detected by our saccharimeter, so the effect of differences in concentrations has been neglected and the average value of column XII. used in the following calculations:

The values in Table B hold only for the temperature of 20°.

Table B.

20°.

Weight-normality. I.	Grams of cane-sugar in 1000 grams water. II.	Percentage concentration. III.	$[\alpha]_D^{20}$ for cane-sugar. IV.	Grams invert-sugar in 100 cc. of solution. V.	$[\alpha]_D^{20}$ for invert-sugar. VI.
0.10	33.96	3.284	66.431	0.10-1.00	-19.67
0.20	67.92	6.360	66.466	0.10-1.00	-19.67
0.30	101.88	9.246	66.491	0.10-1.00	-19.67
0.40	135.84	11.959	66.508	0.10-1.00	-19.67
0.50	169.80	14.515	66.520	0.10-1.00	-19.67
0.60	203.76	16.927	66.526	0.10-1.00	-19.67
0.70	237.72	19.206	66.528	0.10-1.00	-19.67
0.80	271.68	21.364	66.525	0.10-1.00	-19.67
0.90	305.64	23.409	66.520	0.10-1.00	-19.67
1.00	339.60	25.351	66.510	0.10-1.00	-19.67

Ratio VI. to IV. VII.	Grams cane-sugar in 1000 cc. producing 1° rotation. VIII.	Grams of invert-sugar formed from VIII. IX.	Laevorotation of IX. X.	Total loss in rotation. XI.	Grams invert-sugar in 100 cc. = 10 loss in rotation. XII.
0.2961	0.26112	0.27487	0.3117	1.3117	0.20955
0.2959	0.26098	0.27472	0.3115	1.3115	0.20947
0.2958	0.26088	0.27461	0.3114	1.3114	0.20940
0.2958	0.26081	0.27454	0.3113	1.3113	0.20937
0.2957	0.26077	0.27450	0.3113	1.3113	0.20933
0.2957	0.26075	0.27447	0.3113	1.3113	0.20931
0.2957	0.26073	0.27445	0.3113	1.3113	0.20930
0.2957	0.26075	0.27447	0.3113	1.3113	0.20931
0.2957	0.26077	0.27450	0.3113	1.3113	0.20933
0.2957	0.26080	0.27453	0.3113	1.3113	0.20936

The procedure in determining this value for different temperatures is essentially the same as the above. The specific rotatory power of cane-sugar at different temperatures is calculated from the formula¹.

$$[\alpha]_D^t = [\alpha]_D^{20} - 0.0144 (t - 20).$$

¹ Landolt: "Optische Drehungsvermögen," p. 531.

Similar values for invert-sugar are obtained from the formula of Gubbe.¹

$$[\alpha]_D^t = [\alpha]_D^{20} + 0.3041 (t - 20) + 0.00165 (t - 20)^2.$$

Table C contains the results for six different temperatures. Column VIII. contains the quantities of invert-sugar in 100 cc. which correspond to a loss of 1° in rotation.

Table C.

Temperature.	$[\alpha]_D^t$ for cane-sugar. I.	$[\alpha]_D^t$ for invert-sugar. II.	Ratio II. to I. III.	Grams cane-sugar in 100 cc. 1° rotation. IV.
18°	66.53	—20.27	0.3047	0.26072
19°	66.51	—19.97	0.3003	0.26080
20°	66.50	—19.67	0.2958	0.26084
21°	66.49	—19.36	0.2912	0.26088
22°	66.47	—19.06	0.2867	0.26096
23°	66.46	—18.74	0.2820	0.26100

Temperature.	Grams invert-sugar formed from IV. V.	Laevo- rotation of V. VI.	Total loss in rotation. VII.	Grams invert- sugar in 100 cc. 1° loss in rotation. VIII.
18°	0.27445	0°.3207	1°.3207	0.20780
19°	0.27453	0°.3160	1°.3160	0.20861
20°	0.27457	0°.3114	1°.3114	0.20937
21°	0.27462	0°.3065	1°.3065	0.21019
22°	0.27470	0°.3018	1°.3018	0.21102
23°	0.27474	0°.2968	1°.2968	0.21186

In order to apply this to our experiments, it is necessary to know the amount of invert-sugar contained in every 1000 grams of water in any given solution of cane-sugar, since the solutions of which the osmotic pressure was measured were made up on this basis.

In order to make this transformation to the weight-basis, the values in column VIII. must be multiplied by one-tenth the volumes of the corresponding solutions. These columns were found from the specific gravities interpolated from the values given by Morse² and Frazer.

¹ Landolt, *Optische Drehungsvermögen*, p. 531.

² Am. Chem. J., 34, 1.

The results of this calculation are given in Table D.

Table D.

Invert-sugar in grams per 1000. Grams of water producing a loss of 1° in rotation.

Weight-normal concentration.	Temperature.					
	18° .	19° .	20° .	21° .	22° .	23° .
0.10	2.12	2.13	2.14	2.15	2.15	2.16
0.20	2.16	2.17	2.18	2.19	2.20	2.21
0.30	2.21	2.22	2.23	2.23	2.24	2.25
0.40	2.25	2.26	2.27	2.28	2.29	2.30
0.50	2.31	2.32	2.32	2.33	2.34	2.35
0.60	2.34	2.35	2.36	2.37	2.38	2.38
0.70	2.38	2.39	2.40	2.41	2.42	2.43
0.80	2.43	2.44	2.44	2.45	2.46	2.47
0.90	2.47	2.48	2.49	2.51	2.51	2.52
1.00	2.51	2.52	2.53	2.54	2.55	2.56

The above tables have been tested experimentally and the values given shown to hold satisfactorily. Reference has already been made to the publication of these experimental results.

The correction for inversion may now be easily made by simply determining the rotation in a two-decimeter tube of some of the original solution, which must be reserved for the purpose, and of the solution from the cell. The loss in rotation in degrees is multiplied by the value taken from the table for the given concentration at the temperature of polarization. This gives the concentration of invert-sugar in grams per 1000 grams of water. The osmotic pressure that would be produced by one-half this quantity of invert-sugar is the correction that must be deducted from the observed osmotic pressure.

Correction for Dilution of Cell Contents.¹

There must be some dilution of the cell contents, due to the small quantity of water drawn in from the cell wall during the manipulation of attaching the manometer to the cell, also to any slight increase in the capacity of the cell under pressure, and to the rise of the mercury in the manometer. Experience and calculations as to the extent of dilution, due to these sources, indicate that it is very small. Small as this dilution is at

¹ For fuller discussion of this subject see *Am. Chem. J.*, 36, 48-53.

most, it is nearly entirely obviated by the practice of following up the development of the osmotic pressure with mechanical pressure on the stopper, produced by screwing down the nut carried by the manometer. This almost entirely removes the dilution that would be produced by the rise of the mercury in the manometer. A calculation of the amount of this dilution in the most extreme case met with, showed that it corresponded to less than 0.01 atmosphere in pressure. Screwing down the nut of the manometer is also necessary to give rigidity to the joint of the manometer and cell.

A source of dilution which must sometimes be taken into account is that produced by the slipping of the manometer in the stopper. This movement is measured by the rise in the top of the manometer, which sometimes takes place to the extent of a millimeter or two, though usually to a much less extent. In experiments where an abnormal rise of the top of the manometer takes place it is also observed that the loss in rotation of the solution is greater and the osmotic pressure lower than in the case of experiments with solutions of the same concentration, where this movement of the manometer is much less. This is just what is to be expected.

In such experiments this dilution may be corrected for on the basis of other experiments of like concentration where the manometer remained comparatively rigid. The loss in rotation in the latter experiments is regarded as the normal loss for inversion in this concentration and the former experiment is corrected for inversion with this value. The excess loss in rotation in the experiment where there was a slipping of the manometer is calculated as loss in concentration of the solution in cane-sugar, and its value in pressure is calculated and added to the observed pressure. Experiments corrected in this way fall in line with those which do not require this correction. No experiments in which it was necessary to apply this correction for dilution are recorded in the present work.

Other Corrections.

In all observations on the mercury column the hair of the micrometer was set on the edge of the mercury column and the

proper correction applied for the meniscus, assuming it to be hemispherical in the small bore of the manometer.

To the sugar solutions, of which the pressure was measured, was added 0.0839 gram of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ per 100 grams of water. The solvent which surrounded the cell contained 1.2392 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per 1000 grams of water. These concentrations of membrane formers are not isotonic. However, as it was uncertain whether their exact influence on the pressures measured could be easily determined, and as these concentrations were used in the previous measurements, it was decided to continue their use, that the results might be comparable. No correction has been applied for their influence, as preliminary experiments indicate that the problem is one of some complexity. In the lower concentrations their influence is probably most felt and amounts roughly to 0.05 atmosphere pressure on the interior of the cell.

The deviation of Boyle's law for air below pressures of 25 atmospheres has been considered carefully, and owing to the extremely slight magnitude, and to the meagre and unsuitable data for determining its extent, and further to the compensating effect of the temperature coefficient of air under such pressures, it has been decided to disregard its influence in the calculations below.

In regard to the expansion of the walls of the manometer it might simply be stated that the distance between the top of the manometer and the bottom scratch, when the instrument was under the greatest pressure measured, was identical with this distance measured where the manometer was not subjected to pressure.

Any fermentation of the products of inversion within the cell would, of course, affect the pressure. No evidence of such fermentation, however, has ever been observed.

In the form of manometer used, small quantities of air must be condensed against the walls of the tube as the mercury column rises, but there seems no satisfactory method of determining its amount, though it is surely very small.

When the cell contents are under pressure, the mercury thread is forced over into the bulb on the descending arm, which has

many times the diameter of the bore of the manometer tube, so a correction must be applied for capillary depression. The amount of this correction has been determined and applied as recorded in the tables.

The question of the distribution of the water taken into the cell through the membrane has been considered and for several reasons it was decided not to attempt to procure a more equal distribution of this water by stirring or otherwise. First, as has already been pointed out, the entire amount of water taken into the cell is very small. Second, no observations were made which indicated that maximum pressures were not registered.¹

General and Theoretical Considerations.

When accurate measurements of the osmotic pressures of solutions were secured in this laboratory, it was at once noticed that the values obtained departed widely from the theoretical gas pressures calculated on the basis that "*Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume.*"²,—a basis which seems to have been regarded as the proper one for the comparison, according to the hypothesis of van't Hoff, of osmotic pressure and gas pressure. Under such circumstances, it is evident either of two courses must be pursued. The discrepancies must be regarded as abnormalities and reconciled in some way with the values derived from the gas laws, or else a new basis must be found for the consideration of osmotic pressure. The former course is the one which has hitherto been followed, though no satisfactory way has yet been presented for accounting for these abnormalities.

If, on the other hand, the mass of the solvent is taken into consideration, as it does not seem to have been done previous to the work in this laboratory, a new basis may be established which places the values for osmotic pressures and gas pressures in very close agreement throughout the entire series of concentrations studied in this work, that is, if the volume at which the gas pressure is to be calculated is regarded not as the vol-

¹ For fuller discussion of this question, see *American Chemical Journal*, 36, 47, 48.

² "Solutions," Ostwald (Trans. by Muir), London, 1891.

ume of the solution, but as the volume of the solvent at its temperature of maximum density, the discrepancies between the values for osmotic pressures and corresponding gas pressures will disappear.

In accordance with this idea, the solutions studied below have been prepared by dissolving sub-multiples of the gram-molecular weight of cane-sugar in 1000 grams of water, thus defining the volume of our gas as the unit volume, 1 litre. Such solutions are hereafter designated as weight-normal solutions, to distinguish them from solutions prepared by dissolving the given substance in water and diluting up to a litre. It is evident, of course, that the volumes of weight-normal solution, prepared in the above manner, are greater than 1 litre.

The gas pressures are then calculated by finding the pressures which corresponding concentrations of hydrogen gas would exert when enclosed in 1 litre volume, at the temperatures of the solutions, with the osmotic pressures of which they are to be compared.

For example, to prepare a 1.0 weight-normal solution of cane-sugar, 339.6 grams of sugar ($H = 1$) are dissolved in 1000 grams of water, and the corresponding gas pressure found by calculating the pressure exerted by 2 grams of hydrogen gas when reduced to 1 litre volume, at the temperature at which the osmotic pressure of the solution is measured. Thus, taking Morley's value 0.089826 gram for the weight of 1 litre of hydrogen, under standard conditions of temperature and pressure, reduced to the latitude of this place, we have

$$\frac{2.00}{0.089826} = 22.265 \text{ atmospheres at } 0^\circ \text{ or at any higher tem-}$$
 peratures $22.265 (1 + 0.00367 t)$ or $22.265 + 0.0817 t$, atmospheres, for the gas pressure corresponding to the osmotic pressure of a weight-normal solution at the temperature t ; that is, if the weight-normal solution exerts an osmotic pressure equal to the pressure of a gram-molecular weight of a gas reduced to 1 litre volume, and if osmotic pressure like gas pressure obeys the law of Gay-Lussac, its osmotic pressure should be 22.265 atmospheres at 0° or $22.265 + 0.0817 t$, atmospheres at any higher temperature.

Consequently, if the osmotic pressure, p , which any solution is found to exert at the temperature t , is divided by $22.265 + 0.0817 t$, the quotient is the concentration of the solution in terms of the weight-normal system, that is,

$$\frac{P}{22.265 + 0.0817 t} = \text{weight-normal concentration of any solution.}$$

To find the molecular weight, m , of any solution from the osmotic pressure, P , which a known weight of it, W , exerts when dissolved in 1000 grams of water, we have only to ascertain the

value of M in the proportion $\frac{P}{22.265 + 0.0817 t} : 1 :: W : M$.

The formula for the calculation of molecular weight from osmotic pressure is, therefore, $M = \frac{W(22.265 + 0.0817 t)}{P}$.

The measurements given in the following tables have been tested by this formula and the results given in the last column of each table.

Experimental Part.

The cell used in these experiments and designated by G, was before baking, of the following dimensions: Length 9.12 cm., diameter of opening 2.51 cm., exterior diameter below rim 3.58 cm. After baking the dimensions were: Length, 8.25 cm., exterior diameter at top just below rim 3.20 cm., exterior diameter at bottom 2.60 cm., interior diameter at top 2.28 cm. The cell had a capacity of 15.3 cc. after the stopper bearing the manometer had been inserted.

The cell having been constructed as described, was made ready for use by the deposition on its inner surface of a semi-permeable membrane of copper ferrocyanide. This was the kind of membrane used throughout the work.

Preliminary, however, to the deposition of the membrane, the air must be removed from the porous wall of the cell. To accomplish this, advantage was taken of the "electrical endosmose" of dilute salt solutions. For this purpose a glass tube having the same diameter as the neck of the cell, and about 10 cm. long, provided with a smaller side tube for the overflow,

was attached to the neck of the cell with a stout rubber connection. A smaller tube, provided with a reservoir at one end and closely wrapped with a platinum electrode at the other, was passed through a stopper in the larger tube and extended almost to the bottom of the cell. A heavy platinum wire, running up the side of the smaller tube and passing out through the cork, joined the electrode to a binding post on the stand holding the apparatus. The cell was held suspended in a jar by means of a clamp attached to the stand, and surrounded with a large platinum electrode, which was connected with the other binding post on the stand.

The outside vessel and the cell were filled with a 0.005 normal solution of lithium sulphate. The electrolyte formerly used was a solution of potassium sulphate of the same concentration, but the lithium salt was found preferable, as it produced a much more rapid endosmose.

The purpose of the reservoir attached to the smaller tube was to renew the solution within the cell from time to time, since this accelerates the endosmose. The side tube was to provide for the overflow of the solution which was caught and measured. The amount of this overflow is an indication of the texture of the cell wall.

A potential of 110 volts was employed and the current passed through the cell from the outside. At first the current was 0.54 ampere and the overflow very rapid, amounting to about 50 cc. the first hour. In several hours, however, the current fell to 0.025 ampere and the overflow decreased to 7 cc. per hour, and later to 5 cc. About 140 cc. were passed through the cell wall before the air was regarded as being entirely displaced. This method of removing the air from the cell wall was supplemented by immersing the cell in recently boiled distilled water. An endosmose as small as this is unusual and indicates a very dense texture. In cells used in other parts of this work, endosmose of 20 cc. to 30 cc. was obtained, while in the cells used in this laboratory last year it amounted to as much as 40 cc. per hour. This density of texture is also indicated by other characteristics which will be pointed out later.

After the air is removed from the porous wall the electro-

lyte is replaced by distilled water and the current closed, frequent renewals being made until the electrolyte is completely removed. This generally requires about 12 hours.

The cell is now ready for the deposition of the membrane. For this purpose the same apparatus was employed as was used for the removal of the air from the cell wall, substituting for the platinum anode surrounding the cell one of copper. A 0.1 solution of copper sulphate was placed in the outer vessel containing the copper anode and the cell was filled with a 0.1 normal solution of potassium ferrocyanide. A potential of 110 volts was found most suitable for the deposition of this membrane.

The solution of potassium ferrocyanide within the cell was renewed every five minutes to prevent the accumulation of alkali, which is injurious to the membrane. In the deposition of membranes this must not be neglected. The strength of the current was read every ten minutes, though usually at five-minute intervals in the initial deposition, in order to secure information regarding the formation of the membrane. The current passing through a good cell after the formation of the membrane has commenced is small, and was read with a Weston's direct reading mill-ammeter.

The potential of the current used in the deposition of membranes must be very steady. The source of the current employed in this work was a storage battery of 72 cells, which could be arranged so as to give the desired voltage.

The record of the initial deposition of the membrane will be given to show the course of its formation.

Record.

February 6, 1906.

Time.	Current.	Voltage.	Resistance.
3:10 P.M.	0.0010	106	106000
3:20 "	0.0014	106	75714
3:25 "	0.0020	106	53000
3:30 "	0.0022	106	48181
3:35 "	0.0022	106	48181
3:40 "	0.0022	106	48181
3:45 "	0.0023	106	46304
3:50 "	0.0030	106	35500

Time.	Current.	Voltage.	Resistance.
4:00 "	0.0043	106	24767
4:10 "	0.0047	106	22660
4:20 "	0.0047	106	22660
4:30 "	0.0045	106	23660
4:40 "	0.0042	106	25357
4:50 "	0.0035	106	30428
4:55 "	0.0031	106	34354

It will be noticed that the current was much greater at the moment of closing than at any other time, and rapidly decreased to a much smaller amount, as shown in the second reading only two minutes later. Observing the resistance it will be seen that it began high and decreased for a while, reaching a minimum, after which it began to increase again. The explanation of this seems obvious. At first the cell wall was saturated with pure water, and offered great resistance to the passage of the current, but soon, under the influence of the current, the ions of the electrolyte penetrated the wall, greatly increasing its conductivity. As the ions met, the membrane was built up and the resistance again increased.

After this membrane deposition the cell was placed in distilled water and the membrane allowed to soak till next day, when it was again subjected to the membrane-forming process.

Record.

February 7, 1906.

Time.	Current.	Voltage.	Resistance.
2:50	0.0057	108.0	18947
3:00	0.0014	107.7	76928
3:10	0.0010	107.7	107700
3:20	0.0010	107.7	107700
3:30	0.0010	107.6	107600
3:40	0.0010	107.4	107400
3:50	0.0010	107.4	107400
4:00	0.0011	107.4	97636
4:10	0.0011	107.4	97636

Here the resistance was lower than at the conclusion of the first deposition, though it increased very rapidly and reached a maximum, which it maintained for 40 minutes. This is a typical example of the conduct of a membrane after its initial deposition.

The high resistance here is an indication of improvement in the strength of the membrane, and it will be noticed that subsequent depositions raised this maximum of resistance still higher and maintained it for a much longer period.

Record.

February 8, 1906.

Time.	Current.	Voltage.	Resistance.
2:50 P.M.	0.0013	108.5	83461
3:00 "	0.0007	108.5	155000
3:10 "	0.0005	108.2	216400
3:20 "	0.0004	108.2	270500
3:30 "	0.0004	108.2	270500
3:40 "	0.0004	108.2	270500
3:50 "	0.0004	108.2	270500
4:00 "	0.0004	108.2	270500
4:10 "	0.0004	108.2	270500
4:20 "	0.0004	108.2	270500
4:30 "	0.0004	108.2	270500

After this deposition the membrane was thought to be in a suitable condition to be subjected to a development of osmotic pressure. The cell was rinsed and filled with a half weight-normal cane-sugar solution, containing potassium ferrocyanide in 0.1 normal quantity. The manometer was attached and the cell was supported in a bottle containing a 0.1 normal copper sulphate solution. A pressure of 5.4 atmospheres was developed in 3 hours and afterwards dropped slowly to about 2 atmospheres. The pressure normal to this solution was about 12 atmospheres at the temperature of this experiment.

The membrane was undoubtedly ruptured by the pressure. This is what usually happens when a cell is set up for the first time, and it is only after the weak points are thus developed and repaired by further membrane depositions, etc., that the membrane is suitable for quantitative measurements. The cell was then taken down, and after careful rinsing was filled with distilled water and allowed to stand in a vessel of water until all the sugar was abstracted from the membrane and the cell wall. This procedure was always observed whenever a cell

had been used, since no satisfactory maximum can be secured when the cell wall contains sugar.

It might be said here that whenever the cell was not in use it was filled with distilled water and placed in a basin of the same, though, of course, the water is not allowed to cover the cement joint. This is one of the many essential details which must be carefully looked after, since if the cell wall or membrane is ever allowed to dry out, it is seriously injured.

After soaking several hours the cell was again subjected to the membrane-forming process.

The resistance of the membrane at the start was only 5550 ohms, showing that the membrane had been injured in the experiment. A maximum of 42000 ohms was reached after one and a half hours.

The cell was then soaked over night and the membrane reinforced again next morning. It reached a maximum of 151000 ohms in 30 minutes. It was placed in distilled water until the afternoon of February 13, and again subjected to the membrane-forming process.

The very low resistance, at the start of only 5550 ohms, indicated that the membrane had been seriously ruptured by the pressure in the above experiment. This was soon patched up, however, and the resistance rose in a very few minutes to over 20,000 ohms. Further, the membrane was much strengthened by the subsequent depositions, as was indicated by the higher maxima reached.

These features of the membrane-forming process are pointed out, as they illustrate the way in which the membranes are developed and strengthened. In all subsequent work the same plan was adhered to. After every experiment the membrane was soaked in distilled water and reinforced by subjection to the membrane-forming process. The cell was never set up for a quantitative measurement without such treatment of the membrane and was always set up soon after a satisfactory maximum had been reached. The records of these membrane reinforcements will not be given here, but the maximum resistance obtained before each experiment is recorded in the accompanying tables.

After the membrane had been developed to a high degree of efficiency, a single reinforcement, after an experiment, was usually ample to place the membrane in a condition for another experiment. The greater the number of depositions, however, a membrane is subjected to, the more efficient it becomes. Cells thus increase greatly in value with use.

After the membrane reinforcement on February 13th, the cell was again set up for measurement with a solution of the same concentration as that used in the first experiment. The cell was set up in the afternoon and by the next morning it had developed a pressure of 12.30 atmospheres. The theoretical value was about 12.00 atmospheres for the temperature of this experiment. Of course, this experiment was not to be regarded as exactly quantitative, as the solution was prepared only approximately half weight-normal, and no particular precautions were taken to control the temperature. This pressure was maintained until the cell was taken down.

This experiment was regarded as indicating that the cell was in good condition for accurate measurements. The first quantitative experiment attempted was with a 0.6 weight-normal solution.

The cell, after the second preliminary experiment, was soaked and the membrane reinforced in the usual manner. It was then set up with an accurately prepared 0.6 weight-normal solution, but the membrane-formers were used in only 0.01 normal concentration, instead of 0.10 normal concentration, as was used in the preliminary experiments. This was a much severer test for the membrane, both because the pressure to which it was subjected was greater and the membrane-formers were used in much less concentration, hence the membrane could not patch as readily when minute ruptures occurred. The results of this experiment came a little low though, considering the severe conditions, this was regarded as very favorable conduct. Such experiments were repeated until the membrane was developed to a point where quite satisfactory results were secured. Space cannot be devoted here to the details of these first experiments, though several points of importance brought out by them will be mentioned.

It was soon observed that the cell possessed most remarkable characteristics. The maximum of resistance increased from one treatment of the membrane to another and soon reached a value of 300,000 ohms. It has been customary heretofore to regard resistances of 100,000 to 150,000 ohms as very high. From these records, then, unusual qualities were to be expected in the conduct of the cell in the development of pressure, and such proved to be the case. Pressures were developed with great rapidity and maximum values reached in from 6 to 8 hours.

That maximum values were certainly reached in this interval was shown definitely by several experiments, which were allowed to remain up from 50 to 75 hours, and in no case was there a sensible increase in pressure after the first 8 hours. This point was of importance, since it was desirable not to leave the cell contents under pressure any longer than was necessary to make certain that maximum values had been reached.

The experiments recorded below, with the exception of the 0.9 weight-normals, which were not carried out in cell G, show maximum pressures in about 8 hours, and it was customary to leave the cell under this pressure for about 12 hours before taking it down.

Before proceeding to remarks concerning the individual measurements, a few words will be said in regard to the manipulation in attaching the manometer to the cell. The selection and attachment of the rubber stopper to the manometer has already been mentioned. This must be attended to at least 24 hours before the manometer is placed in use. The mercury, which completely filled the end of the manometer bearing the stopper, was replaced around to the bulb, with some of the solution of which the pressure was to be measured.

The cell was then taken from the membrane deposition apparatus, rinsed carefully with water and a number of times with the solution of which the pressure was to be measured, with which it was finally filled. The stopper carrying the manometer was pressed against the neck of the cell and then crowded into the neck by means of a flange, made by first sawing a groove down the side of the untempered end of a

round file, and then grinding the end into the form of a cylinder or wire. This manipulation required two workers, one to manage the manometer and cell the other to operate the flange. When the stopper was well started into the cell the flange was removed, and the stopper forced in until several atmospheres pressure was indicated in the manometer, when the flange was inserted down the side of the stopper against the glass tube and some of the solution was forced out and the pressure relieved. The flange was now removed and the stopper forced in again, etc., until it was inserted far enough. The pressure on the stopper must not be relieved at all while the flange is inserted down the side of the tube, for if it is, air bubbles will be sucked into the cell. This operation requires much strength and skill, since any awkward movement might destroy the labor of weeks.

When the stopper was inserted the part extending above the neck of the cell was wrapped tightly with waxed shoemaker's thread and afterwards with sticky insulating tape. Next, the nut on the manometer was drawn down on the stopper and the brass collar slipped over the cell and screwed on the nut, drawing the latter down closely on the top of the stopper. The cell was then supported in a bottle by means of a cork, as shown in Fig. I. The cork contained a slit for the communication of atmospheric pressure to the liquid in the bottle.

As soon as the pressure showed a tendency to increase, the collar was screwed up farther on the nut. After the stopper adjusted itself, the collar was screwed up still more until it seemed certain that the stopper was supported sufficiently to withstand the pressure of the solution.

The bottle containing the cell was then placed before the cathetometer, and readings were taken of the level of the solution in the bottle and of the surface of the solution and mercury in the bulb (the solution being forced around into the bulb by the mechanical pressure placed on the cell contents), the bottom scratch, the height of the mercury in the manometer and the top of the manometer. These readings enable one to calculate the pressure due to the column of solution in the manometer, that is, the difference in level of the solution in

the bottle and in the bulb, in terms of millimeters of mercury, and also to calculate the mercury pressure at any subsequent reading of the pressure of the cell, by adding the distance of the scratch above the surface of the mercury in the bulb to the height of the mercury above the bottom scratch, correcting this column for temperature and expressing it in terms of atmospheres. The sum of the mercury pressure and the hydrostatic pressure of the solution in the arm of the manometer gave the correction for "Liquids in Manometer," recorded in column VII. of the tables. This correction must be added to the actual gas pressure in the manometer. The readings of the mercury column and the top of the manometer enable one to calculate the mechanical pressure, which has been placed on the cell contents and which is recorded under "Initial Pressure" in the tables.

The cell is now placed in the can located in the temperature bath, as already described. Readings were taken about every four hours on the mercury column and the top of the manometer.

The records of the individual experiments are given in the accompanying tables.

A list of values used in the computations is as follows:

The atomic weight of hydrogen equals 1.

The molecular weight of cane-sugar equals 339.6.

Temperature coefficient of gases equals 0.00367.

Temperature coefficient of mercury equals 0.0001818.

Weight of 1 litre of hydrogen at Baltimore equals 0.089829 gram.

Pressure exerted by a gram-molecular weight of hydrogen gas when reduced at 0°, to a volume of 1 litre equals 22.265 atmospheres.

All weights used in this work have been reduced to vacuum.

The purity of the sugar employed was established by determining the rotation of solutions of known concentration, also by direct combustion and the determination of the hydrogen and carbon, and by the demonstration from time to time, both by means of Fehling's test and the saccharimeter, of the absence of products of inversion. Samples of the sugar employed

in our experiments, when thus tested, were found to be of a degree of purity quite satisfactory.

Measurements have been made in this work of solutions of 0.1, 0.3, 0.5, 0.7, and 0.9, weight-normal concentrations. The intermediate even-numbered concentrations through the normal were measured by Mr. E. J. Hoffman, who has assisted me in the many manipulations in this work which required two operators. The results obtained by him will be quoted in connection with the summary of the values obtained in this work.

Tables¹ I. and II.

0.1 weight-normal solution—Experiments 1 and 2.

Weight of cane-sugar dissolved in 1000 grams of water equals 33.960 grams.

Specific gravity of solution at 20° equals 1.01283.

Volume of solution at 20° equals 1020.86 cc.

0.0839 gram of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ was dissolved in the sugar solution and the solution which surrounded the cell was prepared by dissolving 1.2392 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 1000 grams of water. These concentrations of membrane-formers were used in all the following experiments.

Of the corrections given in the tables, those of "Liquids in Manometer" and "Capillary Depression" are added to the gas pressure in the manometer, found by dividing the corrected final air volume into the total air volume of the manometer under standard conditions, while the "Atmospheric Pressure" and "Inversion" are to be deducted, in order to ascertain the "Osmotic Pressure Corrected."

It will be observed that the molecular weights in these two experiments came rather low. This was because a mistake of 0.10 atmosphere produces a much greater effect on the calculated molecular weight in dilute solutions than in concentrated ones. Thus, in this concentration, 0.10 atmosphere corresponds to about 14 points in the calculated molecular weight, while

¹ The actual readings by the telescope have been omitted from the tables on account of the large amount of space they would occupy, though the records have been made sufficiently complete to permit of a recalculation of the results.

the same pressure in a 0.9 weight-normal solution only corresponds to 1.55 units in the molecular weight.

The pressures in these two experiments were rather high. An explanation of at least a part of this excess pressure is to be found in the pressure of the membrane-formers, which preliminary experiments have shown, when they are present in the pure solvent, to exert about 0.07 atmosphere pressure. How the presence of large quantities of sugar affect their dissociation is unknown; however, it is reasonable to say that its influence is least in dilute solutions.

In Experiment 1 the top of the manometer rose only 0.07 mm. In Experiment 2 it amounted to 0.54 mm. Movements in the top of the manometer amounting to less than 2 mm. are too small to justify a correction for dilution on the basis already explained. Such movements may represent a slipping of the manometer in the stopper, though they are of a sufficiently small magnitude to be explained to a large extent by the adjustment of the bottle containing the cell in the can. Such a movement of the manometer has only had a measurable effect on the pressures and caused abnormal loss in rotation of the solution within the cell, in instances where it amounted to as much as 2 mm. or more, though these smaller movements undoubtedly indicate a slight dilution. However, that the dilution is small is indicated by the fact that the difference in this movement of the manometer in these two experiments, which was 0.47 mm. produced a dilution too small to affect the loss in rotation in the two experiments, which amounted to 0.5 in both cases.

Tables III. and IV.

0.3 weight-normal solution—Experiments 1 and 2.

Weight of cane-sugar dissolved in 1000 grams of water equals 101.880 grams.

Specific gravity of solution at 20° equals 1.03687.

Volume of solution at 20° equals 1062.70 cc.

Membrane-formers of the same concentration as before.

In Experiment 1, the maximum pressure was reached in 4 hours, and in Experiment 2, the pressure was practically at a maximum also in 4 hours, though it was not so regarded

in the calculations until the second reading 4 hours later. In Experiment 1 the top of the manometer lifted only 0.12 mm. and in Experiment 2, 0.10 mm.

The effect of a mistake of 0.10 atmosphere in this concentration, on the calculated molecular weight equals 4.72 units.

Tables V. and VI.

0.5 Weight-normal solution—Experiments 1 and 2.

Weight of cane-sugar dissolved in 1000 grams of water equals 169.800 grams

Specific gravity of solution at 20° equals 1.05900.

Volume of solution at 20° equals 1104.62 cc.

Membrane-formers of the same concentration as before.

In Experiment 1 the top of the manometer raised 0.16 mm., in Experiment 2, 0.32 mm.

The effect of a mistake of 0.10 atmosphere, in this concentration, on the calculated molecular weight equals 2.80 units.

Tables VII. and VIII.

0.7 Weight-normal solution—Experiments 1 and 2.

Weight of cane-sugar dissolved in 1000 grams of water equals 273.720 grams.

Specific gravity of solution at 20° equals 1.07947.

Volume of solution at 20° equals 1146.60 cc.

Membrane-formers of the same concentration as before.

It might be added here that in several of the preceding experiments the solution on the outside of the cell was, after the experiment, carefully examined for traces of sugar to determine whether there was any leakage of the sugar through the membrane, but in every case examined there could not be found a trace of sugar.

Further, in several experiments the rotation of the solution was determined just after it was prepared and was found to be the same as the rotation after it had stood till the experiment was taken down. This shows that no inversion takes place in the solution while it is not under pressure in the cell.

In Experiment 1, the top of the manometer rose 0.24 mm., and in Experiment 2, 0.07 mm.

The effect of a mistake of 0.10 atmosphere in this concentration on the calculated molecular weight equals 2.00 units.

Tables IX. and X.

0.9 weight-normal solution—Experiments 1 and 2

Weight of cane-sugar dissolved in 1000 grams of water equals 305.640 grams.

Specific gravity of the solution at 20° equals 1.09833.

Volume of solution at 20° equals 1188.75 cc.

Membrane-formers of the same concentration as before.

In Experiment 1, the top of the manometer rose 1.21 mm., in Experiment 2, 0.87 mm.

The effect of a mistake of 0.10 atmosphere, in this concentration, on the calculated molecular weight equaled 1.55 units.

When cell G, with which all the previous experiments have been made, was set up for measurement with a 0.9 weight-normal solution, about the time the pressure had reached a maximum the glass tube of the cell broke. On taking the cell down a crack was found, which extended the entire length of the tube. This, of course, rendered the cell useless for further pressure measurements.

On account of the remarkable characteristics of this cell, it was prized highly, and most painstaking efforts have been made to repair it without the removal or injury of the membrane but the results of this undertaking are as yet uncertain.

The copper ferrocyanide membrane may be readily dissolved by alkaline tartrate solution, though after removing a membrane in this way and freeing the cell wall of electrolytes, if a new membrane is deposited it is generally inferior to the first one. On this account such a course was not resorted to in repairing this cell, though it would have rendered its repair a comparatively simple matter.

The two experiments of this concentration were measured with cells A and B; the ones with which the measurements by Morse and Frazer were made last year.

These cells, it will be observed from the tables, had much lower resistance than G and were longer in reaching a maximum.

Table III.

Original wt. normal concentration of solution, 0.3. Experiment No. 1.
 Rotation of original solution, $36^{\circ}.5$ ($t = 19^{\circ}$). Manometer used, No. 6.
 Rotation at conclusion of experiment, 36° ($t = 19^{\circ}$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $0^{\circ}.5$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 275,000 ohms.
 Time of setting up cell, 4.00 P. M., March 14, 1906. Initial pressure, 3.50 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.					
March 14.													
8.15 P. M.	21°.55	22°.10	56.91										
11.50 "	21°.60	22°.30	56.65	52.37	1.00	0.62	0.07	0.02	7.25	+0.04	337.68		
March 15.													
10.45 A. M.	21°.70	22°.04	56.80	52.55	0.99	0.62	0.07	0.02	7.23	+0.02	338.72		338.37
3.00 P. M.	21°.70	22°.24	56.84	52.55	0.99	0.62	0.07	0.02	7.23	+0.02	338.72		

Table V.

Original wt. normal concentration of solution, 0.5. Experiment No. 1.
 Rotation of original solution, 59° ($t = 20^\circ$). Manometer used, No. 6.
 Rotation at conclusion of expt., 57.6 ($t = 20^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, $1^\circ.4$. Cell used, G.
 Calibration units of air in manometer, 402.13. Resistance of membrane, 274,500 ohms.
 Time of setting up cell, 4.30 P. M., March 19, 1906. Initial pressure, 10.80 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.					Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.		
March 19.												
8.30 P. M.	$22^\circ.60$	$22^\circ.80$	34.61									
11.30 "	$22^\circ.65$	$22^\circ.50$	34.55	31.92	0.98	0.65	0.22	0.02	12.07	12.06	+0.01	339.26
March 20.												
8.00 A. M.	$22^\circ.50$	$22^\circ.50$	34.55	31.92	0.99	0.65	0.22	0.02	12.06	12.05	+0.01	339.36
11.30 "	$22^\circ.70$	$22^\circ.60$	34.62	31.97	0.99	0.65	0.22	0.02	12.04	12.06	-0.02	340.16

Table VII.

Original wt. normal concentration of solution, 0.7.	Experiment No. 1.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
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Original wt. normal concentration of solution, 0.7. Experiment No. 1.
 Rotation of original solution, 79°.1 ($t = 22^\circ$). Manometer used, No. 4.
 Rotation at conclusion of expt., 76°.5 ($t = 22^\circ$). Capillary depression, 0.02 atmosphere.
 Loss in rotation, 2°.6. Cell used, G.
 Calibration units of air in manometer, 461.34. Resistance of membrane, 222,000 ohms.
 Time of setting up cell, 5.00 P. M., March 26, 1906. Initial pressure, 9.63 atmospheres.

Table VIII.

Original wt. normal concentration of solution, 0.7.

Experiment No. 2.

Rotation of original solution, $79^{\circ}.2$ ($t = 19^{\circ}$).

Manometer used, No. 6.

Rotation at conclusion of expt., 77° ($t = 19^{\circ}$).

Capillary depression, 0.02 atmospheres.

Loss in rotation, $2^{\circ}.2$.

Cell used, G.

Calibration units of air in manometer, 402.13.

Resistance of membrane, 280,000 ohms.

Time of setting up cell, 4.30 P. M., March 30, 1906.

Initial pressure, 9.49 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Theoretical gas pressure.	Difference b'tween pressure found and calculated.	Molecular weight calculated from osmotic pressure.	Mean molecular weight.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.			
March 30. 8.30 P. M.	$23^{\circ}.74$	$23^{\circ}.80$	24.80	22.81	0.98	0.67	0.36	0.02	16.98	$+0.09$	338.87	
March 31. 12.00 A. M.	$23^{\circ}.74$	$24^{\circ}.00$	24.85	22.84	0.98	0.67	0.36	0.02	16.96	$+0.07$	339.27	
9.00 "	$23^{\circ}.80$	$24^{\circ}.00$	24.84	22.83	0.98	0.67	0.36	0.02	16.97	$+0.02$	339.14	339.50
12.30 P. M.	$24^{\circ}.30$	$23^{\circ}.90$	24.94	22.89	0.98	0.67	0.36	0.02	16.92	-0.06	340.70	

Table IX.

Time.	Temperature.		Air in manometer.		Volume of air in manometer.		Corrections.					Molecular weight.		
	Solution.		Uncorrected.		Corrected.		Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure, corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.	Molecular weight calculated from osmotic pressure.
May 1.														
8.00 P. M.	24° 00	24° 50	28.27											
May 2.														
10.30 A. M.	24° 00	24° 20	22.03											
6.30 P. M.	24° 20	25° 15	21.87											
May 3.														
10.00 A. M.	24° 65	25° 30	21.53	19.70	0.99	0.66	0.43	0.02	21.71	21.85	—0.14	341.81		
1.00 P. M.	24° 70	25° 30	21.50	19.67	0.99	0.66	0.43	0.02	21.73	21.85	—0.12	341.55		
5.30 "	24° 80	25° 30	21.43	19.61	0.99	0.66	0.43	0.02	21.81	21.86	—0.05	340.41		
11.00 "	24° 90	25° 35	21.35	19.37	0.99	0.66	6.43	0.02	21.90	21.87	+0.03	339.12		340.19
May 4.														
10.30 A. M.	24° 90	24° 50	21.22	19.32	0.99	0.66	0.43	0.02	21.97	21.87	+0.10	338.04		

Original wt. normal concentration of solution, 0.9.
 Rotation of original solution, 98° ($t = 22^\circ$).
 Rotation at conclusion of expt., 95° 5 ($t = 22^\circ$).
 Loss in rotation, 2° 5.
 Calibration units of air in manometer, 442.18.
 Time of setting up cell, 1.00 P. M., May 1, 1906.
 Initial pressure, 10.40 atmospheres.

Experiment No. 1.
 Manometer used, No. 5.
 Capillary depression, 0.02 atmosphere.
 Cell used, A.
 Resistance of membrane, 64, 100 ohms.

Table XI.—Summary of Results.

Weight-normal concentration of solution.	Osmotic pressure observed (atmospheres).	Gas pressure calculated for same temperature (atmospheres).	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weight mean values.
<i>Experiment 1.</i>					
0.1	2.50	2.41	+0.09	329.09	327.85
	2.50	2.41	+0.09	329.14	
	2.52	2.42	+0.10	326.58	
	2.52	2.42	+0.11	326.58	
<i>Experiment 2.</i>					
	2.53	2.42	+0.11	325.40	322.56
	2.56	2.42	+0.14	321.58	
	2.56	2.43	+0.13	321.63	
	2.56	2.43	+0.13	321.63	
<i>Experiment 1 (Hoffman).</i>					
0.2	4.73	4.79	—0.06	343.93	344.96
	4.73	4.79	—0.06	344.16	
	4.71	4.79	—0.08	345.76	
	4.71	4.80	—0.09	345.99	
<i>Experiment 2 (Hoffman).</i>					
	4.81	4.80	+0.01	338.85	340.90
	4.80	4.80	0.00	339.67	
	4.79	4.80	—0.01	340.38	
	4.76	4.80	—0.04	342.58	
	4.76	4.80	—0.04	343.02	
<i>Experiment 3 (Hoffman).</i>					
	4.81	4.81	0.00	339.37	339.74
	4.81	4.81	0.00	339.54	
	4.80	4.81	—0.01	340.31	

Table XI. (continued).

Weight-normal concentration of solution.	Osmotic pressure observed (atmospheres).	Gas pressure calculated for same temperature (atmospheres).	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights mean values.
<i>Experiment 1.</i>					
0.3	7.25	7.21	+0.04	337.68	338.37
	7.23	7.21	+0.02	338.72	
	7.23	7.21	+0.02	338.72	
<i>Experiment 2.</i>					
	7.21	7.16	+0.05	337.36	338.18
	7.21	7.16	+0.05	337.53	
	7.17	7.17	0.00	339.70	
<i>Experiment 1 (Hoffman).</i>					
0.4	9.62	9.61	+0.01	339.17	338.73
	9.64	9.61	+0.03	338.61	
	9.64	9.61	+0.03	338.72	
	9.65	9.61	+0.04	338.43	
<i>Experiment 2 (Hoffman).</i>					
	9.69	9.63	+0.06	337.44	337.50
	9.69	9.63	+0.06	337.50	
	9.69	9.63	+0.06	337.55	
<i>Experiment 1.</i>					
0.5	12.07	12.06	+0.01	339.29	339.59
	12.06	12.05	+0.01	339.36	
	12.04	12.06	-0.02	340.16	
<i>Experiment 2.</i>					
	12.19	12.10	+0.09	337.11	336.19
	12.25	12.10	+0.15	335.46	
	12.23	12.10	+0.13	336.01	
<i>Experiment 1 (Hoffman).</i>					
0.6	14.70	14.55	+0.15	336.14	335.32
	14.74	14.55	+0.19	335.35	
	14.76	14.55	+0.21	334.89	
	14.76	14.55	+0.21	334.89	

Table XI. (continued).

Weight-normal concentration of solution.	Osmotic pressure observed (atmospheres).	Gas pressure calculated for same temperature (atmospheres).	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights mean values.
<i>Experiment 2 (Hoffman).</i>					
	14.69	14.54	+0.15	336.20	
	14.70	14.55	+0.15	336.03	
	14.71	14.55	+0.16	335.90	
	14.70	14.55	+0.15	336.13	336.06
<i>Experiment 3 (Hoffman).</i>					
	14.74	14.54	+0.20	335.00	
	14.77	14.54	+0.23	334.32	
	14.79	14.54	+0.25	333.87	
	14.78	14.54	+0.24	334.10	
	14.77	14.54	+0.23	334.32	334.32
<i>Experiment 1.</i>					
0.7	16.99	16.92	+0.07	338.39	
	16.94	16.92	+0.02	339.39	
	16.96	16.95	+0.01	339.40	
	16.92	16.96	-0.04	340.37	339.39
<i>Experiment 2.</i>					
	16.98	16.89	+0.09	338.87	
	16.96	16.89	+0.07	339.27	
	16.97	16.95	+0.02	339.14	
	16.92	16.98	-0.06	340.70	339.49
<i>Experiment 1 (Hoffman).</i>					
0.8	19.30	19.35	-0.05	340.53	
	19.26	19.35	-0.09	341.27	
	19.29	19.35	-0.06	340.73	
	19.33	19.35	-0.02	340.03	
	19.34	19.35	-0.01	339.85	340.48
<i>Experiment 2 (Hoffman).</i>					
	19.35	19.36	-0.01	339.79	
	19.31	19.36	-0.05	340.49	
	19.43	19.36	+0.07	338.39	
	19.44	18.36	+0.08	338.22	
	19.42	19.36	+0.06	338.51	339.08

Table XI. (Continued).

Weight-normal concentration of solution.	Osmotic pressure observed (atmospheres).	Gas pressure calculated for same temperature (atmospheres).	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights mean values.
<i>Experiment 1.</i>					
0.9	21.71	21.85	-0.14	341.81	
	21.73	21.85	-0.12	341.55	
	21.81	21.86	-0.05	340.41	
	21.90	21.87	+0.03	339.12	
	21.97	21.87	+0.10	338.05	338.42
<i>Experiment 2.</i>					
	21.86	21.85	+0.01	339.47	
	21.88	21.85	+0.03	339.21	
	21.92	21.86	+0.06	338.70	
	21.98	21.87	+0.11	337.89	
	22.05	21.87	+0.18	336.82	340.18
<i>Experiment 1 (Hoffman).</i>					
1.0	24.47	24.19	+0.28	335.70	
	24.49	24.19	+0.30	335.45	335.57
<i>Experiment 2 (Hoffman).</i>					
	24.05	24.28	-0.23	342.78	
	24.06	24.28	-0.22	342.66	342.72

Table XII.—Mean Molecular Weight for Each Concentration.

Concentration.	Molecular weight.
0.1	325.21
0.3	338.28
0.5	337.89
0.7	339.44
0.9	339.30
Mean value	336.02
Mean for even concentrations	338.82
Mean of two series	337.42
Theoretical value	339.60
Difference	2.18

Conclusions.

The conclusions to which the foregoing experiments seem to lead have been presupposed in the calculation of the theoretical gas pressures with which the observed values have been compared. The close agreement between these values confirms the conclusion of Morse and Frazer, that "Cane-sugar dissolved in water exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state." Whether the correct standard is the volume of the solvent at the temperature of maximum density or at some other temperature, such as the temperature at which the pressure is measured, the measurements are hardly sufficiently refined to decide, since in the most concentrated solutions studied the theoretical values, calculated on the basis of the volume of the solvent at the temperature of maximum density, are only 0.06 atmosphere higher than the values calculated on the basis of the volume of the solvent at the temperature at which the pressure is measured. However, it may be said that the observed values of the osmotic pressure of the solutions were usually even higher than those calculated on the basis of the volume of the solvent at the temperature of maximum density, a fact which favors the latter basis as the proper one for the comparison of osmotic pressure and gas pressure.

From this it appears that in the analogy between solutions and gases, the mass of the pure solvent plays the important rôle of determining the volume in which the dissolved substance must be contained in the form of a gas to exert the same pressure that it exerts in the form of osmotic pressure in the larger volume of the solution.

BIOGRAPHY.

The author of this work, William Lee Kennon, was born in Columbus, Mississippi, May 3, 1882. He received his early training under private tutors, and in 1895 he entered the preparatory school of Millsaps College, being admitted to the collegiate department the following year. In 1900 he received the degree of bachelor of science from that institution. In 1901 he was appointed instructor of geology at Millsaps, and in the same year he received the degree of master of science, chemistry being the principal subject for that degree. At the close of 1901 he was appointed professor of chemistry in Kentucky Wesleyan College, where he remained two years. In the fall of 1903 he entered the graduate department of the Johns Hopkins University, making chemistry his principal subject, and physical chemistry and physics first and second subordinate subjects, respectively. In 1904-1905 he held a University scholarship and in 1905-1906 he held a Fellowship in Chem-

istry.

The results obtained hardly seem capable of explanation on any other basis than that the membrane does not adhere firmly to the cell wall and is easily detached either during manipulation or while under pressure. This view explains the sudden fall in pressure which so often occurred after the pressure had begun to rise at a good rate, as in Experiment II. with cell J. On the other hand, it often happened that after a development of pressure, on a repetition of the same preliminary treatment, the membrane not only failed to show improvement but gave poorer results than in the first case, as for instance in experiments VI. and VII. with cell K, conduct which is also capable of explanation on the above view.

Again, the ease with which the membrane could be detached from the cell by simple agitation with water is a further indication of the imperfect manner in which it is attached to the cell wall. It might be added that the membrane removed in this way had a flaky appearance, an observation which seemed to confirm the conclusion that in the experiments recorded either the manipulation in attaching the manometer to the cell or the pressure developed within the cell detached portions of the membrane or ruptured the membrane itself. The best results were obtained in Experiment V. with Cell J, and in experiment VI. with cell K, though in both cases attempts to further improve the membranes by the same treatment which had been employed in these experiments proved fruitless.

It might, therefore, be concluded that zinc ferrocyanide, deposited under the conditions employed in this work, cannot be deposited on the rather dense walls of the cells used in a form suitable for the measurement of high osmotic pressures.

The experience in working with this membrane, together with the experience in the development of the copper ferrocyanide membrane employed in the first part of this work, has impressed the author with the importance of carefully developing and thorough testing of all membranes, to make sure of their strength and activity under the particular conditions under which they are to be employed before proceeding to the measurement of osmotic pressure.

This experiment alone is sufficient to demonstrate that the cell was in good condition. Moreover, this conduct of the cell was repeated in subsequent experiments.

Table XIII.—Summary of Results.

Cell J. Zinc Ferrocyanide Membrane.									
No. of mem- brane rein- forcements before exp.	Maximum resistance of mem- brane.	Weight normality of solu- tion.	Normality of mem- brane pres- sure.	Approx- imate the- oretical osmotic pressure.	At- mospheres.	Vol- tage used.	No. of Hxp.		
I.	2	43,000	0.50	0.10	2.75	12.00			
II.	1	40,000	0.50	0.10	5.46	12.00			
III.	1	60,000	0.10	0.00	0.00	2.40			
IV.	2	56,900	0.10	0.10	0.00	2.40			
V.	1	60,800	0.50	0.10	5.74	12.00			
VI.	2	46,000	0.50	0.10	2.52	12.00			
VII.	2	49,700	0.50	0.10	1.52	12.00			
VIII.	2	39,300	0.50	0.50	2.96	12.00			
Cell J. Copper Ferrocyanide Membrane.									
IX.	2	121,400	0.50	0.10	12.02	11.96			
Cell K. Zinc Ferrocyanide Membrane.									
I.	4	48,000	0.50	0.10	1.00	12.00			
II.	3	41,500	0.50	0.10	1.09	12.00			
III.	3	51,300	0.50	0.10	0.00	12.00			
IV.	37.5	28,700	0.50	0.10	1.43	12.00			
V.	2	23,400	0.50	0.10	1.81	12.00			
VI.	4	14,700	0.50	0.10	6.95	12.00			
VII.	4	15,600	0.50	0.10	1.03	12.00			
Cell K. Copper Ferrocyanide Membrane.									
VIII.	110	110,000	0.50	0.10	11.97	12.00			
Conclusions.									

The foregoing experiments show that a semipermeable mem-
brane of zinc ferrocyanide can be readily deposited by means of
the electric current on a porous wall, separating solutions of
zinc sulphate and potassium ferrocyanide. They further show
that such a membrane possesses decided osmotic activity, as
was pointed out by Carver. However, the membranes deposited
under the conditions employed in this work seem unsuitable
for the measurement of high osmotic pressures.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equaled 110 volts. Cell set up at 4:50 P.M., February 14, 1906. The mercury column began to rise at once, and by 10:30 P.M., a corrected osmotic pressure of 11.97 atmospheres had been reached, which was maintained until the cell was taken down the next day.

Experiment VIII.

As the time which could be devoted to this investigation was exhausted the experiments were discontinued. The zinc ferrocyanide membrane was replaced with a membrane of copper ferrocyanide. The maxima of resistance obtained with the latter membrane were 106,300 ohms, 86,000 ohms and 110,000 ohms.

February 3, 1906. The maximum pressure in this experiment was 1.03 atmospheres. The cell was left up 12 hours after this pressure was reached, but no further increase took place. This conduct was entirely unexpected, and on examination of the solution on the outside of the cell it was found that sugar had leaked through the membrane.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equaled 12 volts. Cell set up at 5:00 P.M.,

Experiment VII.

After such a small increase in pressure during the last 48 hours it was not thought advisable to allow the cell to remain up longer, though the experiment as a whole seemed encouraging, since there was such a decided improvement over any previous experiment with this cell. It was hoped that the employment of the lower voltage might lead to the successful development of the membrane. The course now adopted was to thoroughly repair the membrane by reinforcing it a number of times before trying another experiment. The maxima obtained in these depositions were 13,000 ohms, 15,000 ohms, 24,000 ohms, and 15,600 ohms.

the resistances were not so high as those previously obtained. Three membrane depositions were made before the cell was set up for a measurement. The maxima obtained were 24,900 ohms, 37,400 ohms, and 28,700 ohms.

Experiment IV.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equalled 37.5 volts. Cell set up at 3:10 P.M., January 17, 1906.

Pressure developed very slowly and only reached a maximum of 1.43 atmospheres after 20 hours. As this change of voltage seemed to have no decided influence on the activity of the membrane, a still lower potential was employed. That selected was about 12 volts. The maxima obtained here were 14,200 ohms and 23,400 ohms.

Experiment V.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equalled 12 volts. Cell set up at 5:00 P.M., January 19, 1906.

Time.	Osmotic pressure corrected.	Atmospheres.
Jan. 20, 11:40 A.M.	1.81	
" 22, 11:00 A.M.	1.37	

The cell was left up till 11:00 A.M., January 23rd, but no sensible change in pressure occurred. The membrane was reinforced again at 12 volts, giving a maxima of 14,700 ohms.

Experiment VI.

0.10 weight-normal solution. 0.10 normal membrane-formers. Potential equalled 12 volts. Cell set up at 5:30 P.M., January 25, 1906.

Time.	Osmotic pressure corrected.	Atmospheres.
Jan. 25, 10:45 P.M.	2.40	
" 26, 10:45 A.M.	4.80	
" " 7:50 P.M.	5.88	
" 27, 10:45 A.M.	6.33	
" 28, 11:50 A.M.	6.61	
" 29, 10:15 A.M.	6.95	

Observations.

10:40 A.M. next day and showed no tendency to rise again. When the subsequent membrane deposition was made, the membrane gave the usual low resistance at the start, amounting to only 6,000 ohms, indicating that the membrane, even under the low pressure of this experiment, had been badly ruptured or detached.

It was at this point that it was decided to change from 75 volts to 110 volts for the deposition of the membrane. The maxima of resistance with the larger potential were 28,000 ohms, 36,000 ohms, and 41,500 ohms respectively.

Experiment II.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equalled 110 volts. Cell set up at 5:00 P.M., January 11, 1906.

Pressure was developed very slowly and only reached 1.09 atmospheres by 10:30 A.M., next day. There seemed no further tendency for a change at this time, so the cell was taken down and allowed to soak in distilled water for some time. The membrane was then reinforced again at a voltage of 110. The maxima obtained in the three depositions made were 47,800 ohms, 77,400 ohms, and 51,300 ohms. The cell was then set up for a pressure measurement.

Experiment III.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equalled 110 volts. Cell set up at 4:45 P.M., January 15, 1906.

In this experiment there was no development of pressure. The mechanical pressure placed on the cell contents in attaching the manometer soon subsided and there was no further change.

In rinsing the cell, after taking it down, the wash water was found to have a slightly milky appearance, which was shown to be due to the presence of some of the detached membrane. A lower voltage than any of those previously used was then employed for the further treatment of the membrane. The potential selected was 37.5 volts. With this lower voltage

by the presence of 0.10 normal membrane-formers, which experiment has shown produces about 0.72 atmospheres pressure, and the inversion correction which amounts to about 0.20 atmosphere. This would give for the corrected osmotic pressure of the above experiment 12.05 atmospheres. Thus, with the copper ferrocyanide membrane, a theoretical pressure was obtained and this pressure of over twelve atmospheres was maintained in the cell in which the zinc membrane had given such unsatisfactory results. This experiment alone was sufficient to show that there was no imperfection in the construction of the cell.

This record with the copper ferrocyanide membrane was most remarkable for the first experiment. Unfortunately, however, at the conclusion of the experiment the glass neck of the cell cracked in such a way that the cell could not be brought into use again.

Cell K.

This cell gave an electrical endosmose of 48 cc. per hour when the air was driven from the cell wall. This indicated a texture more porous than either of the previous cells. The potential used in the initial deposition of the membrane was 75 volts. The plan adopted in this case was to subject the cell repeatedly to the membrane-forming process before setting it up for the first experiment. The records were quite normal and only the maxima will be given. They were 22,500 ohms, 35,300 ohms, 41,000 ohms, and 48,000 ohms respectively.

Experiment I.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equaled 75 volts. Cell set up at 12 M., January 9, 1906. About 1 atmosphere pressure was placed on the cell contents, after which the mercury column began to rise slowly. The pressure soon afterwards began to fall slowly and continued until atmospheric pressure was reached. The cell was left up till

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equaled 110 volts. Cell set up at 5:00 P.M., January 24, 1906. Membrane of copper ferrocyanide. The mercury column in the manometer began to rise rapidly and at 7:15 P.M. a pressure of 8.80 atmospheres had been reached. This rose to a maximum of 12.97 atmospheres by 9:40 P.M., which was maintained for some time. The theoretical pressure for this experiment was 11.96 atmospheres. The excess pressure in this experiment can be easily accounted for

Experiment IX.

The cell was set up for a measurement. 120,400 ohms. At the conclusion of this membrane deposition in the cell in the usual manner. The resistance of the copper ferrocyanide was much higher than that of the zinc ferrocyanide membrane. The maximum after two depositions was out. The copper ferrocyanide membrane was then deposited of electrolysis. In this way the cell wall was thoroughly cleaned potassium hydroxide. The last traces were removed by means while most of what remained was dissolved out with dilute means of a soft brush a much larger amount was detached in which the precipitate was attached to the cell wall. By tity of the membrane and indicated the very imperfect way and violently agitated. This treatment detached a large quantity. First, however, the cell was partly filled with water-ubility of zinc ferrocyanide in dilute sodium hydroxide solution of the cell. For this purpose advantage was taken of the section of the membrane and not to any fault in the construction the unsatisfactory results obtained above were due to the imperfection of the membrane and not to any fault in the construction of the cell. The next course was to replace the zinc ferrocyanide membrane with one of copper ferrocyanide in order to show that the unsatisfactory results obtained above were due to the imperfection of the membrane and not to any fault in the construction of the cell. For this purpose advantage was taken of the solubility of zinc ferrocyanide in dilute sodium hydroxide solution. First, however, the cell was partly filled with water and violently agitated. This treatment detached a large quantity of the membrane and indicated the very imperfect way in which the precipitate was attached to the cell wall. By means of a soft brush a much larger amount was detached while most of what remained was dissolved out with dilute potassium hydroxide. The last traces were removed by means of electrolysis. In this way the cell wall was thoroughly cleaned out. The copper ferrocyanide membrane was then deposited in the cell in the usual manner. The resistance of the copper ferrocyanide was much higher than that of the zinc ferrocyanide membrane. The maximum after two depositions was 120,400 ohms. At the conclusion of this membrane deposition the cell was set up for a measurement.

Potential equaled 110 volts. Cell set up at 5:30 P.M., January 18, 1906. At 7:30 P.M. the pressure was 2.34 atmospheres; at 11:00 P.M. it had increased to 2.96 atmospheres. The next day at 10:45 A.M. the pressure had fallen to 1.43 atmospheres. After this experiment no further efforts to develop the zinc ferrocyanide membrane were made.

Observations.

Osmotic pressure corrected.
Atmospheres.

Dec. 21,	Time.
" 22, 9:00 A.M.	1.04
" " 2:40 P.M.	1.38
" " 4:45 P.M.	1.43
" 23, 10:00 A.M.	2.52

After the last observation the cell was removed from the solvent, the surface dried and about six atmospheres pressure placed on the cell contents. It was thought in this way any leak in the membrane might be discovered. However, no evidence of sugar having leaked through the membrane could be obtained.

After these experiments it was decided, in view of the very unsatisfactory results, to try a potential of 110 volts instead of 75 volts in the hope that better results might be obtained. The membrane was deposited several times at this voltage before a measurement was attempted. This change in voltage did not affect the magnitude of the maxima obtained to any considerable extent. The values obtained on successive membrane depositions were 35,500 ohms, 45,800 ohms, and 49,700 ohms. The cell was then set up for a pressure measurement.

Experiment VII.

0.50 weight-normal solution. 0.10 membrane-formers. Potential equaled 110 volts. Cell set up at 4:35 P.M., January 17, 1906.

The mercury column began to rise very slowly and after 18 hours reached 1.52 atmospheres. Owing to this unfavorable conduct the cell was taken down, and after soaking in distilled water its membrane was reinforced again. It gave a maximum of 39,300 ohms. The cell was then set up for another experiment. This time it was decided to try the influence of more concentrated membrane-formers.

Experiment VIII.

0.50 weight-normal solution. 0.50 normal membrane-formers.

Experiment V.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equalled 75 volts. Cell set up at 5:00 P.M., December 18, 1905.

At 9:00 P.M. a pressure of about 2 atmospheres had been developed. Next day at 10:30 A.M. the pressure had increased to 3.48 atmospheres and continued to rise slowly, but although the cell was left up for a considerable length of time, the pressure gave little promise of ever reaching a maximum. A complete list of the observations taken are as follows:

Observations.

Time.	Osmotic pressure corrected. Atmospheres.
Dec. 18, 9:00 P.M.	2.00
" 19, 10:30 A.M.	3.48
" " 2:30 P.M.	3.63
" " 4:45 P.M.	4.47
" " 11:30 P.M.	5.01
" 20, 10:30 A.M.	5.64
" " 2:30 P.M.	5.69
" " 4:00 P.M.	5.74

The small increase of 0.10 atmosphere in the interval of 16 hours, over which the last three observations extended, could hardly be considered as a promise of higher pressures. The theoretical pressure for this solution was 12.02 atmospheres. The cell seemed to show some improvement, however, and it was decided to continue the same plan of work.

The cell was taken down and placed in distilled water. When its membrane was reinforced again, it showed a resistance of only 6,100 ohms at the start and increased in two hours to 38,900 ohms. The cell was allowed to soak several hours in distilled water and its membrane reinforced again. This time a maximum of 46,000 ohms was reached. The cell was again set up for measurement.

Experiment VI.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equalled 75 volts. Cell set up at 4:30 P.M., December 21, 1905.

When the membrane was again reinforced the resistance was found to be very low, as it was after the first experiment, and amounted to 8,900 ohms. The resistance rose in two hours to 38,000 ohms, when the cell was placed in distilled water. The membrane was reinforced again the next day and the maximum raised to 60,000 ohms. The cell was again set up for a pressure measurement. This time it was decided to give the membrane gentler treatment by using a more dilute solution.

Experiment III.

0.10 weight-normal solution. No membrane-formers were used. Potential equalled 75 volts. Cell set up at 12:40 P.M., December 15, 1905.

After the cell had been placed in the outside solution, a gentle pressure was placed on the stopper in order to support it. Immediately the mercury column began to fall slowly and in an interval of several hours had reached atmospheric pressure, where it remained until the cell was taken down twelve hours later. On again subjecting the membrane to the membrane-forming process, as measured by its resistance, it was found to be in fairly good condition, giving a resistance of 33,500 ohms at the start, and increasing in 20 minutes to a maximum of 56,900 ohms. The previous experiment was repeated with the use of 0.10 normal membrane-formers.

Experiment IV.

0.10 weight-normal solution. 0.10 normal membrane-formers. Potential equalled 75 volts. Cell set up at 4:30 P.M., December 16, 1905.

In this experiment there was no pressure developed. The pressure which had been exerted mechanically in attaching the manometer to the cell soon fell to that of the atmosphere and there seemed no tendency to further change. The cell was taken down and the subsequent reinforcement of the membrane gave a maximum of 60,800 ohms. The cell was set up for another measurement.

This conduct was regarded as most promising, and the cell was set up with a 0.50 weight-normal cane-sugar solution, containing 0.10 normal potassium ferrocyanide within the cell and zinc sulphate in the water on the outside.

Experiment I.

0.50 weight-normal solution. 0.10 membrane-formers. Potential equals 75 volts. Cell set up 3:30 P.M., December 7, 1905.

A few minutes after placing the cell in the outside solution the mercury in the manometer began to rise slowly. About 2 atmospheres of mechanical pressure were then placed on the cell contents. Thirty minutes afterwards the pressure had risen to 2.75 atmospheres, when it began to fall, and one hour later amounted to 2.30 atmospheres. It continued to fall until a pressure slightly above that of the atmosphere had been reached.

The cell was then taken down and allowed to stand in distilled water for some time. The membrane was then subjected to the membrane-forming process again. In this deposition the resistance of the membrane at the start was only 5700 ohms, which indicated that the membrane had been badly ruptured in the above experiment. However, it was quickly repaired and the resistance increased in two hours to 40,000 ohms. The cell was again set up for a pressure measurement.

Experiment II.

0.50 weight-normal solution. 0.10 normal membrane-formers. Potential equals 75 volts. Cell set up at 3:15 P.M., December 9, 1905.

After the usual slight fall in the mercury column, due to temperature effects when the cell is first placed in the outside solution, the mercury column began to rise rapidly.

At 5:00 P.M. the pressure was 4.44 atmospheres at 20°; at 9:15 P. M. it had risen to 5.46 atmospheres. The next day at 10:15 A.M. it was observed that the pressure had fallen to 2.94 atmospheres and as it showed no further tendency to change the cell was taken down and placed in distilled water.

two cells, the results can be more conveniently treated under the record of each cell separately.

Experimental Part.

Cell J.

A 0.003 normal solution of lithium sulphate was used to remove the air from the cell wall. The endosmose in this cell amounted to about 40 cc. per hour. Altogether about 200 cc. of solution were passed through the cell wall, and the electrolyte then thoroughly removed. The voltage selected with which to begin work was 75 volts.

The record of the initial deposition is as follows :

Record.

December 6, 1905.

Time.	Current.	Voltage.	Resistance.
1:50 P.M.	0.0046	70.0	15217
2:00 "	0.0046	71.0	15348
2:10 "	0.0045	71.0	15777
2:20 "	0.0050	71.8	14160
2:30 "	0.0047	70.6	15021
2:40 "	0.0041	70.6	17220
2:50 "	0.0037	72.6	19081
3:00 "	0.0033	70.5	21364
3:10 "	0.0032	72.7	22719
3:20 "	0.0031	73.0	23548
3:30 "	0.0029	73.0	25172
3:40 "	0.0026	73.3	28192
3:50 "	0.0025	73.3	29320
4:00 "	0.0024	73.8	30750
4:10 "	0.0023	74.0	32434
4:20 "	0.0022	73.3	32577
4:30 "	0.0022	73.3	32577
4:40 "	0.0022	73.2	32577
4:50 "	0.0021	73.3	34430

The conduct here was similar to that of the copper ferrocyanide membrane, though the initial resistance was not so great. This was due perhaps to the greater porosity of the cell, which was indicated by its rate of endosmose.

The cell was then placed in distilled water until next day, when its membrane was reinforced. The resistance rose in one hour and 20 minutes from 17,000 to 43,000 ohms.

ver merely indicate the osmotic activity of the membrane under pressures slightly above atmospheric pressure, and say nothing regarding its power to withstand high pressures.

Zinc ferrocyanide, $\text{Zn}_2\text{Fe}(\text{CN})_{6.3}\text{H}_2\text{O}$.

Zinc ferrocyanide is formed as a white gelatinous precipitate when aqueous solutions of zinc sulphate and potassium ferrocyanide are brought together. It is insoluble in water and in most mineral acids, especially hydrochloric, sulphuric, and acetic acids. It is readily soluble in solutions of the alkali hydroxides and dissolves in aqueous ammonia, though usually leaving a slight opalescence.

On account of the solubility of the precipitate in potassium hydroxide it is necessary in the electrolytic deposition of the membrane to renew the solution within the cell at frequent intervals. In the following work such renewals were made at intervals of from three to five minutes. The methods employed for the depositions and development of the membranes in this work were essentially the same as those used with the copper ferrocyanide membrane. The solutions used for the purpose of the deposition of the membranes were prepared by dissolving 14.27 grams of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in water and diluting up to 1 litre, and by dissolving 10.49 grams of $\text{K}_4\text{Fe}(\text{CN})_{6.3}\text{H}_2\text{O}$ per litre of solution. The cell was surrounded by an anode of zinc and contained on the interior a cathode of platinum. The cells used were prepared as already described. The method of work was simply to deposit the membranes and, after securing satisfactory maxima of resistance, to set the cells up for measurements with solutions of cane-sugar, usually 0.5 weight-normal, though occasionally with other concentrations. The concentration of membrane-formers was changed from time to time to determine their influence in strengthening the membrane, and finally the membranes were deposited at different potentials to determine the influence of this factor.

Two cells were used in this work and are designated as cell J and cell K. The same manometers employed in the previous work were also used here.

Though the work was carried on simultaneously with the

A STUDY OF ZINC FERROCYANIDE AS A SEMI-PERMEABLE MEMBRANE FOR THE MEASUREMENT OF OSMOTIC PRESSURE

INTRODUCTORY REMARKS.

This membrane was used successfully by Tammann¹ in his optical method for the determination of relative osmotic pressures. Later, Carver², working with Morse, showed that this membrane could be deposited electrolytically by the method of Morse and Horn³. He further made a study of its osmotic activity measured in terms of the rate of endosmose which it produced, which was determined by measuring the amount of solution delivered, under certain conditions, from the vessel in which the membrane was deposited. He also attached an open manometer to the cell in several cases and measured the pressure developed. The membrane studied in this way gave very satisfactory results, and proved to be one of the most active studied by these investigators.

In the deposition of this membrane 0.1 normal solutions of zinc sulphate and potassium ferrocyanide were employed. An anode of zinc surrounded the cell and a cathode of platinum was placed within it. At the conclusion of the deposition the voltage of the current was 108 volts, though the operation was begun at a much lower potential.

In view of the satisfactory conduct of zinc ferrocyanide membrane when worked with according to the above method, it was hoped that it might prove more satisfactory than the copper ferrocyanide membrane, which has been used almost exclusively heretofore in the measurement of osmotic pressure. Or, at least, that the zinc membrane might prove efficient under conditions which prohibit the use of a copper membrane. Though it must be remembered that the experiments of Car-

¹ *Wied. Ann.*, 34, 229 (1888).

² B. F. Carver, Dissertation, Johns Hopkins Univ. (1903).

³ *Am. Chem. J.*, 26, 80.

